Quantum Mechanics

CONTENTS

Unit *Page Nos.*

Unit-I: Mathematical Functions and Standard Integrals ..... (1-8)

Unit-II: Concepts of Classical Mechanics ..... (9-23)

Unit-III: Mathematical Formulation & Postulates of Quantum Mechanics ..... (24-27)

Unit-IV: Bound States Problem ..... (28-78)

Unit-V: Angular Momentum Algebra ..... (79-94)

Unit-VI: Identical Particles ..... (95-101)

Unit-VII: Scattering Theory ..... (102-106)

Unit-VIII: Time Independent Perturbation Theory ..... (107-139)

Unit-IX: Relativistic Quantum Mechanics ..... (140-144)

UNIT - I

MATHEMATICAL FUNCTIONS AND STANDARD INTEGRALS

A. One-Dimensional Delta Function:

Various Definitions of the Delta Function:

The delta function can be defined as the limit of $\delta^{(\varepsilon)}(x)$ when $\varepsilon \to 0$ (Figure 1.1.):

$$\delta(x) = \lim_{\varepsilon \to 0} \delta^{(\varepsilon)}(x), \tag{1.1}$$

Where

$$\delta^{(\varepsilon)}(x) = \begin{cases} 1/\varepsilon, & -\varepsilon/2 < x < \varepsilon/2 \\ 0, & |x| > \varepsilon/2 \end{cases} \tag{1.2}$$

The delta function can be defined also by means of the following integral equations:

$$\int_{-\infty}^{+\infty} f(x)\delta(x)dx = f(0), \tag{1.3}$$

$$\int_{-\infty}^{+\infty} f(x)\delta(x-a)dx = f(a), \tag{1.4}$$

We should mention that the $\delta-$functions is not a function in the usual mathematical sense. It can be expressed as the limit of analytical functions such as

$$\delta(x) = \lim_{\varepsilon \to 0} \frac{\sin(x/\varepsilon)}{\pi x}, \qquad \delta(x) = \lim_{a \to \infty} \frac{\sin^2(ax)}{\pi a x^2} \tag{1.5}$$

Or, $$\delta(x) = \lim_{\varepsilon \to 0} \frac{1}{\pi} \frac{\varepsilon}{x^2 + \varepsilon^2} \tag{1.6}$$

The Fourier transform of $\delta(x)$, which can be obtained from the limit of $\frac{\sin(x/\varepsilon)}{\pi x}$, is:

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx} dk, \tag{1.7}$$

Which in turn is equivalent to

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx} dk = \frac{1}{2\pi} \lim_{\varepsilon \to 0} \int_{-1/\varepsilon}^{+1/\varepsilon} e^{ikx} dk = \lim_{\varepsilon \to 0} \frac{\sin(x/\varepsilon)}{\pi x} = \delta(x) \tag{1.8}$$

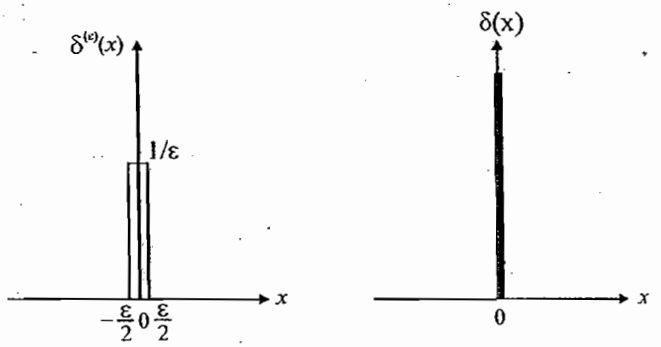


Figure1.1: The delta function $\delta(x)$ as defined by $\delta(x) = \lim_{\varepsilon \to 0} \delta^{(\varepsilon)}(x)$

Properties of the Delta Function:

The delta function is even:

$$\delta(-x)=\delta(x) \qquad \text{and} \qquad \delta(x-a)=\delta(a-x) \tag{1.9}$$

Here are the some of the most useful properties of the delta function:

$$\int_a^b f(x)\delta(x-x_0)\,dx=\begin{cases} f(x_0), & \text{if } a<x_0<b, \\ 0, & \text{elsewhere} \end{cases} \tag{1.10}$$

$$\delta(x)=0 \qquad \text{for } x\neq 0,$$
$$x\delta(x)=0, \tag{1.11}$$

$$\delta(ax)=\frac{1}{|a|}\delta(x) \qquad (a\neq 0) \tag{1.12}$$

$$f(x)\delta(x-a)=f(a)\delta(x-a) \tag{1.14}$$

$$\int_c^d \delta(a-x)\delta(x-b)\,dx=\delta(a-b) \qquad \text{for } c\le a\le d,\ c\le b\le d \tag{1.15}$$

$$\int_a^b \delta(x)\,dx=1 \qquad \text{for} \qquad a\le 0\le b \tag{1.16}$$

$$\delta\left[g(x)\right]=\sum_i \frac{1}{|g'(x_i)|}\delta(x-x_i) \tag{1.17}$$

Where x_i is a zero of g(x) and $g'(x_i)\neq 0$. Using (1.17) we can verify that

$$\delta\left[(x-a)(x-b)\right]=\frac{1}{|a-b|}\left[\delta(x-a)+\delta(x-b)\right] \qquad (a\neq b), \tag{1.18}$$

$$\delta\left(x^2-a^2\right)=\frac{1}{2|a|}\left[\delta(x-a)+\delta(x+a)\right] \qquad (a\neq 0) \tag{1.19}$$

B. Three dimensional Delta Function:

The three-dimensional form of the delta function is given in Cartesian coordinates by

$$\delta(\vec{r}-\vec{r}')=\delta(x-x')\delta(y-y')\delta(z-z')$$

and in spherical coordinates by

$$\delta(\vec{r}-\vec{r}')=\frac{1}{r^2}\delta(r-r')\delta(\cos\theta-\cos\theta')\delta(\varphi-\varphi')$$
$$=\frac{1}{r^2\sin\theta}\delta(r-r')\delta(\theta-\theta')\delta(\varphi-\varphi')$$

Since, according to (1.17) we have $\delta(\cos\theta-\cos\theta')=\delta(\theta-\theta')/\sin\theta$

The Fourier transform of the three-dimensional delta function is:

$$\delta(\vec{r}-\vec{r}')=\frac{1}{(2\pi)^3}\int d^3k e^{i\vec{k}(\vec{r}-\vec{r}')}$$

And $\int d^3r\, f(\vec{r})\delta(\vec{r})=f(0), \qquad \int d^3r f(\vec{r})\delta(\vec{r}-\vec{r}_0)=f(\vec{r}_0)$

The following relations are often encountered:

$$\vec{\nabla}\cdot\left(\frac{\hat{r}}{r^2}\right)=4\pi\delta(\vec{r}), \qquad \nabla^2\left(\frac{1}{r}\right)=-4\pi\delta(\vec{r})$$

Where $\hat{r}$ the unit vector along $\vec{r}$.

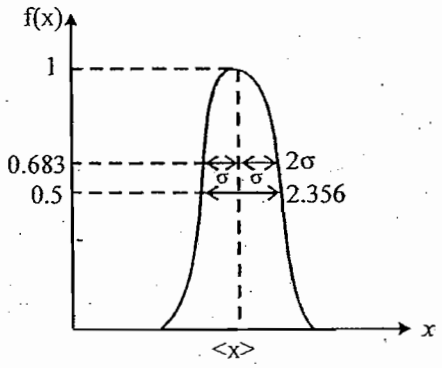
We should mention that the physical dimension of the delta function is one over the dimensions of its argument. Thus, if x is a distance, the physical dimension of $\delta(x)$ is given by $[\delta(x)]=1/[x]=1/L$, where L is a length. Similarly, the physical dimensions of $\delta(\vec{r})$ is $1/L^3$, Since,

$$[\delta(\vec{r})]=[\delta(x)\delta(y)\delta(z)]=\frac{1}{[x]}\frac{1}{[y]}\frac{1}{[z]}=\frac{1}{L^3}$$

C. **Gaussian Function:**

The Gaussian function is defined as

$$f(x)=\frac{1}{\sqrt{2\pi\sigma^2}}e^{\frac{(x-\langle x\rangle)^2}{2\sigma^2}}$$



$\langle x\rangle$ = mean value

σ = Standard deviation
= Root mean square deviation.

D. **Fourier Integral transform:**

If f(x) is a periodic function with a fundamental period L, then it can be expanded in a Fourier series:

$$f(x)=\sum_{n=-\infty}^{\infty}a_n e^{ik_n x} \qquad (1.1)$$

where $k_n=2\pi n/L$. The coefficients a_n of the series are given by

$$a_n=\frac{1}{L}\int_0^L f(x)e^{ik_n x}dx \qquad (1.2)$$

The Fourier transform of a function $f(x)$ is defined as

$$F(k)=F[f(x)]=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(x)e^{-ikx}dx \qquad (1.3)$$

While the inverse Fourier transform is:

$$f(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}F(k)e^{ikx}dk \qquad (1.4)$$

Notice that in quantum mechanics we define the transformations slightly differentily, as follows:

$$\psi(k)=F[\psi(x)]=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x)e^{-ipx/\hbar}dx \qquad (1.5)$$

and

$$\psi(x)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(k)e^{ipx/\hbar}dk \qquad (1.6)$$

Two formulas of Fourier transform theory are especially relevant.

Identity of norms: $$\int_{-\infty}^{\infty}|f(x)|^2\,dx=\int_{-\infty}^{\infty}|F(k)|^2\,dk \qquad (1.7)$$

Parseval's theorem: $$\int_{-\infty}^{\infty}f(x)g^*(x)dx=\int_{-\infty}^{\infty}F(k)G^*(k)dk \qquad (1.8)$$

E. Polynomials

(I) Hermite Polynomials:

The Hermite polynomials $H_n(x)$ are defined by the relation

$$H_n(x)=(-1)^n e^{x^2}\left(\frac{d^n}{dx^n}e^{-x^2}\right) \qquad n=0,1,2..... \qquad (1.1)$$

The $H_n(x)$ are the solution to the differential equation

$$\frac{d^2H_n(x)}{dx^2}-2x\frac{dH_n(x)}{dx}+2nH_n(x)=0 \qquad (1.2)$$

The orthogonality relation for $H_n(x)$ is:

$$\int_{-\infty}^{\infty}e^{-x^2}H_m(x)H_n(x)\,dx=\sqrt{\pi}\,2^n n!\delta_{mn} \qquad (1.3)$$

Two important recurrence relations for $H_n(x)$ are

$$\frac{dH_n(x)}{dx}=2nH_n(x) \qquad H_{n+1}(x)=2xH_n(x)-2nH_{n-1}(x)$$

The first few Hermite polynomials are given below:

$$H_0(x)=1 \qquad H_1(x)=2x \qquad H_2(x)=4x^2-2$$

$$H_3(x)=8x^3-12x \qquad H_4(x)=16x^4-48x^2+12$$

II. Legendre Polynomials:

Legendre polynomials $P_l(x)$ are given by Rodrigue's formula,

$$P_l(x)=\frac{1}{2^n n!}\frac{d^n}{dx^n}\left(x^2-1\right)^n \qquad (1.4)$$

The first Legendre polynomials are given below:

$$P_0(x)=1 \qquad P_1(x)=x \qquad P_2(x)=\frac{1}{2}\left(3x^2-1\right)$$

$$P_3(x)=\frac{1}{2}\left(5x^3-3x\right) \qquad P_4(x)=\frac{1}{8}\left(35x^4-30x^2+3\right)$$

In terms of $\cos\theta$ the first few Legendre polynomials are

$$P_0(\cos\theta)=1 \qquad P_1(\cos\theta)=\cos\theta$$

$$P_2(\cos\theta)=\frac{1}{4}(1+3\cos 2\theta) \qquad P_3(\cos\theta)=\frac{1}{8}(3\cos\theta+5\cos 3\theta)$$

The orthogonality relation of the Legendre polynomials is:

$$\int_{-1}^{1}P_\ell(x)P_{\ell'}(x)\,dx=\frac{2}{2\ell+1}\delta_{\ell\ell'} \qquad (1.5)$$

III. Associated Legendre Functions:

Associated legendre functions $P_\ell^m(x)$ are defined as

$$P_\ell^m(x)=\sqrt{\left(1-x^2\right)^m}\,\frac{d^m}{dx^m}P_1(x) \quad \text{for} \quad -1\le x\le 1 \tag{1.6}$$

Where $m\ge 0$. $P_\ell(x)$ are the Legendre polynomials. Note that

$$P_\ell^0(x)=P_\ell(x) \qquad P_\ell^m(x)=0 \quad \text{for m}>1 \tag{1.7}$$

The differential equation that $P_\ell^m(x)$ satisfies is:

$$\left[\left(1-x^2\right)\frac{d^2}{dx^2}-2x\frac{d}{dx}+\left(\ell(\ell+1)-\frac{m^2}{1-x^2}\right)\right]P_\ell^m(x)=0 \tag{1.8}$$

The first few associated Legendre functions are given below:

$$P_1^1(x)=\sqrt{1-x^2} \qquad P_2^1(x)=3x\sqrt{1-x^2} \qquad P_2^2(x)=3\left(1-x^2\right)$$

$$P_3^1(x)=\frac{3}{2}\left(5x^2-1\right)\sqrt{1-x^2} \qquad P_3^2(x)=15x\left(1-x^2\right) \qquad P_3^3(x)=15\sqrt{\left(1-x^2\right)^3}$$

The orthogonality relation of the associated Legendre functions is:

$$\int_1 P_\ell^m(x)P_{\ell'}^m(x)\,dx=\int_0^\pi P_\ell^m(\cos\theta)P_{\ell'}^m(\cos\theta)\sin\theta\,d\theta=\frac{2}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}\delta_{\ell\ell'} \tag{1.9}$$

IV. Spherical Harmonics:

The spherical harmonics are defined as:

$$Y_\ell^m(\theta,\phi)=(-1)^m\sqrt{\frac{2\ell+1(\ell-m)!}{4\pi(\ell+m)!}}P_\ell^m(\cos\theta)e^{im\phi} \quad \text{for m}\ge 0 \tag{1.10}$$

and

$$Y_1^{-m}(\theta,\phi)=(-1)^m\left[Y_\ell^m(\theta,\phi)\right]^* \tag{1.11}$$

The differential equation that Y_ℓ^m satisfies is:

$$\left[\frac{1}{\sin\theta}\frac{1}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\ell(\ell+1)\right]Y_\ell^m(\theta,\phi)=0 \tag{1.12}$$

The Y_ℓ^m have well-defined parity given as follows:

$$Y_\ell^m(\pi-\theta,\pi+\phi)=(-1)^\ell Y_\ell^m(\theta,\phi) \tag{1.13}$$

The orthonormalization relation of Y_ℓ^m is written as

$$\int_0^{2\pi}d\phi\int_0^\pi\left[Y_{\ell'}^{m'}(\theta,\phi)\right]^* Y_\ell^m(\theta,\phi)\sin\theta\,d\theta=\delta_{\ell'\ell}\delta_{m'm} \tag{1.14}$$

and the closure relation

$$\sum_{\ell=0}^{\infty}\sum_{m=-1}^{\ell}Y_\ell^m(\theta,\phi)\left[Y_\ell^m(\theta',\phi')\right]^*=\delta(\cos\theta-\cos\theta')\delta(\phi-\phi')$$

$$=\frac{1}{\sin\theta}\delta(\theta-\theta')\delta(\phi-\phi') \tag{1.15}$$

Some important recurrence relations are given below:

$$e^{i\phi}\left(\frac{\partial}{\partial\theta}-m\cot\theta\right)Y_\ell^m(\theta,\phi)=\sqrt{\ell(\ell+1)-m(m+1)}\,Y_\ell^{m+\ell}(\theta,\phi) \tag{1.16}$$

$$e^{-i\phi}\left(-\frac{\partial}{\partial\theta}-m\cot\theta\right)Y_\ell^m(\theta,\phi)=\sqrt{\ell(\ell+1)-m(m-1)}\,Y_\ell^{m-1}(\theta,\phi) \tag{1.17}$$

$$Y_\ell^m(\theta,\phi)\cos\theta=\sqrt{\frac{(\ell+1+m)(\ell+1-m)}{(2\ell+1)(2\ell+3)}}Y_{\ell+1}^m+\sqrt{\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}}Y_{\ell-1}^m \tag{1.18}$$

The first few Y_ℓ^m are given below:

$$Y_0^1=\frac{1}{\sqrt{4\pi}}$$

$$Y_1^0=\sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_1^1=-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$$

$$Y_2^0=\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right) \qquad Y_2^1=-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi} \qquad Y_2^2=\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi}$$

$$Y_3^0=\sqrt{\frac{7}{16\pi}}\left(5\cos^3\theta-3\cos\theta\right) \qquad Y_3^1=-\sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta-1\right)e^{i\phi}$$

$$Y_3^2=\sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta e^{2i\phi} \qquad Y_3^3=-\sqrt{\frac{35}{64\pi}}\sin^3\theta e^{3i\phi}$$

An important result for spherical harmonics is:

$$P_l(\cos\alpha)=\frac{4\pi}{2\ell+1}\sum_{m=-1}^{\ell}(-1)^m Y_\ell^m(\theta_\ell,\phi_\ell)Y_\ell^m(\theta_2,\phi_2)$$

Where α is the angle between the directions (θ_1,ϕ_1) and (θ_2,ϕ_2). This result is known as the spherical haronics addition theorem.

V. Associated Laguerre Polynomials:

First we shall deal with the Laguerre polynomials given by Rodrigue's formula,

$$L_\ell(x)=e^x\frac{d^\ell}{dx^\ell}\left(x^\ell e^{-x}\right) \tag{1.20}$$

The associated Laguerre polynomials are defined as

$$L_\ell^m(x)=\frac{d^m}{dx^m}L_\ell(x) \tag{1.21}$$

Where ℓ and m are nonnegative integers, Note that

$$L_\ell^0(x)=L_\ell(x) \qquad L_\ell^0(x)=0 \qquad \text{for } m>1 \tag{1.22}$$

The first few associated Laguerre polynomials are given below:

$$L_1^1(x)=-1 \qquad L_2^1(x)=2x-4 \qquad L_2^2(x)=2$$

$$L_3^1(x)=-3x^2+18x-18 \qquad L_3^2(x)=-6x+18 \qquad L_3^3(x)=-6$$

The orthogonality relation of the associated Laguerre Polynomails is:

$$\int_0^\infty x^m e^{-x}L_\ell^m(x)L_{\ell'}^m(x)\,dx=\frac{(\ell!)^3}{(\ell-m)!}\delta_{\ell\ell'} \tag{1.23}$$

VI. Spherical Bessel Functions:

Bessel's differential equation is given as

$$\left[x^2\frac{d^2}{dx^2}+x\frac{d}{dx}+\left(x^2-\ell^2\right)\right]J_\ell(x)=0 \tag{1.24}$$

Where $\ell \geq 0$. The solutions to this equation are called Bessel functions of order l. $J_\ell(x)$ are given by the series expansion.

$$J_\ell(x)=\frac{x^\ell}{2^\ell\Gamma(\ell+1)}\left[1-\frac{x^2}{2(2\ell+2)}+\frac{x^4}{2.4(2\ell+2)(2\ell+4)}\right]=\sum_{R=0}^{\infty}\frac{(-1)^k(x/2)^{\ell+2k}}{n!\Gamma(\ell+k+1)} \tag{1.25}$$

If $\ell=0,1,2,.....J_{-\ell}(x)=-1^\ell J_\ell(x)$. If $\ell\neq 0,1,2,.....,J_\ell(x)$ and $J_{-\ell}(x)$ are linearly indepdent. In this case $J_\ell(x)$ is bounded at x = 0, while $J_{-\ell}(x)$ is the unbounded Bessel function of the second kind. $N_\ell(x)$ (also called Neumann functions) are defined by

$$N_\ell(x)=\frac{J_\ell(x)\cos(\ell\pi)-J_{-\ell}(x)}{\sin(\ell\pi)} \qquad (\ell\neq 0,1,2,.....) \tag{1.26}$$

These functions are ubounded at x = 0. The general solution of (1.24) is:

$$\begin{cases} y(x)=AJ_\ell(x)+BJ_{-\ell}(x) & \ell\neq 0,1,2..... \\ y(x)=AJ_\ell(x)+BN_\ell(x) & \text{all } \ell \end{cases} \tag{1.27}$$

Where A and B are arbitrary constants. Spherical Bessel functions are related to Bessel functions according to

$$J_\ell(x)=\sqrt{\frac{\pi}{2x}}J_{\ell+\ell/2}(x) \tag{1.28}$$

Also, the Neumann spherical functions are related to the Neumann function $N_\ell(x)$ by

$$n_1(x)=\sqrt{\frac{\pi}{2x}}N_{\ell+\ell/2}(x) \tag{1.29}$$

$J_\ell(x)$ and $n_\ell(x)$ are given explicitly as

$$J_\ell(x)=(-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\left(\frac{\sin x}{x}\right) \tag{1.30}$$

$$n_1(x)=-(-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\left(\frac{\cos x}{x}\right) \tag{1.31}$$

The first few $j_\ell(x)$ and $n_\ell(x)$ are given below:

$$j_0(x)=\frac{\sin x}{x} \qquad n_0(x)=-\frac{\cos x}{x}$$

$$j_1(x)=\frac{\sin x}{x^2}-\frac{\cos x}{x} \qquad n_1(x)=-\frac{\cos x}{x^2}-\frac{\sin x}{x}$$

$$j_2(x)=\left(\frac{3}{x^3}-\frac{1}{x}\right)\sin x-\frac{3}{x^2}\cos x \qquad n_2(x)=-\left(\frac{3}{x^3}-\frac{1}{x}\right)\cos x-\frac{3}{x^2}\sin x$$

The asymptotic behaviour of the $j_\ell(x)$ and $n_\ell(x)$ as $x\to\infty$ and $x\to 0$ is given by

$$\begin{cases} j_\ell(x)_{x\to 0} \to \dfrac{x^\ell}{(2\ell+1)!!} \\ n_\ell(x)_{x\to 0} \to -\dfrac{(2\ell-1)!!}{x^{\ell+1}} \end{cases} \tag{1.32}$$

$$\begin{cases} j_\ell(x)_{x\to\infty} \to \dfrac{1}{x}\sin\left(x-\dfrac{\pi\ell}{2}\right) \\ n_\ell(x)_{x\to\infty} \to -\dfrac{1}{x}\cos\left(x-\dfrac{\pi\ell}{1}\right) \end{cases} \tag{1.33}$$

Where $(2\ell+1)!! = 1.3.5....(2\ell-1)(2\ell+1)$.

$$\int_0^\infty e^{-x}\, x^{n-1} dx = \Gamma n = (n-1)!$$

$$\int_0^\infty e^{-\alpha x} x^n dx = \frac{n!}{\alpha^{n+1}}$$

$$\int_0^\infty e^{-\alpha x^2} x^n dx = \frac{1}{2\alpha^{\left(\frac{n+1}{2}\right)}}\Gamma\left(\frac{n+1}{2}\right);\ n > -1$$

$$\int_{-\infty}^{\infty} e^{-\alpha x^2+\beta x} dx = \sqrt{\frac{\pi}{\alpha}}\, e\frac{\beta^2}{4\alpha}$$

UNIT - II
CONCEPTS OF CLASSICAL MECHANICS:

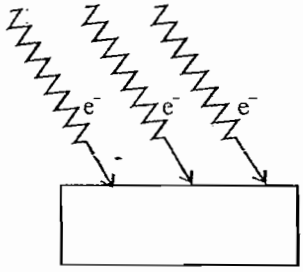
1. According to classical mechanics a particle is separated by energy E and linear momentum P and a wave is specified by amplitude (A) and propagation vector $k = \frac{2\pi}{\lambda}\hat{n}$.

   i.e. $\phi(k) = e^{i\bar{k}.\bar{r}}$ or e^{ikx}

2. According to classical mechanics particle and wave are mutually exclusive.
3. According to classical mechanics all dynamical variable are continuous.
   In classical mechanics energy is related with amplitude but in quantum mechanic energy is related with frequency.
   In classical mechanics information of particle is given by position vector and in quantum mechanics by wave function.

Particle Nature of radiation:
Photo electric effect – ejection of electrons on irradiating any matter.

1. If $\nu < \nu_0$ no ejection of electron (where ν_0 threshold frequency), whatever the intensity of radiation

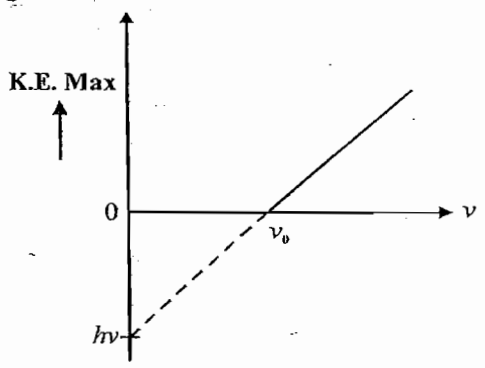


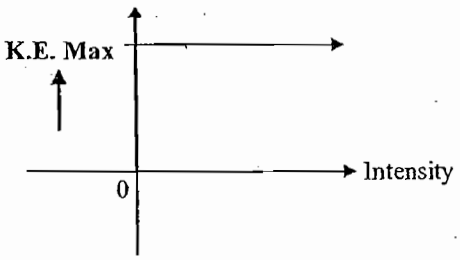
2. If $\nu > \nu_0$ there is always ejection of electrons, whatever be the intensity of radiation.
3. Kinetic energy of ejected electron depends only on the frequency of incident radiation not on the intensity or amplitude.
4. There is no time dilation between incidence of radiation and the ejection of electron $\left(\simeq 10^{-8}\ \text{sec}\right)$.
5. The photo current varies with the intensity of incident radiation.
   According to classical mechanics any radiation can ejected electron whatever be its intensity or frequency. Now if we consider plank's law i.e. $E = nh\nu$ and if one photon is incident the by energy conservation.

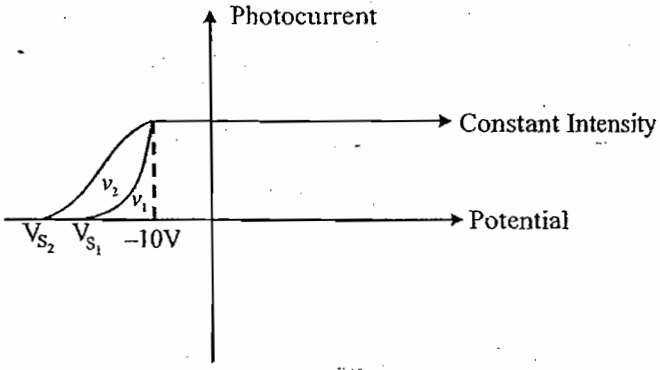
   $$h\nu = h\nu_0 + K.E_{\text{Max}} \quad \Rightarrow \quad K.E_{\text{max}} = h\nu - h\nu_0$$

   If $\nu < \nu_0 \quad \Rightarrow \quad K.E_{\text{max}} = -ve$

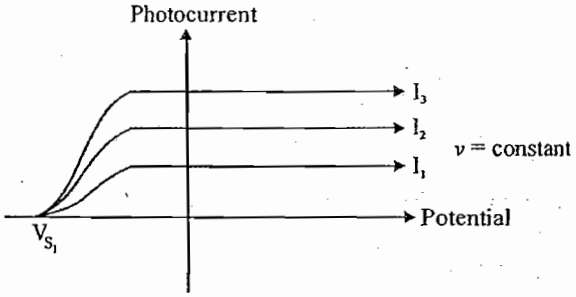
   This –ve energy means this much energy is to be supplied to electron.







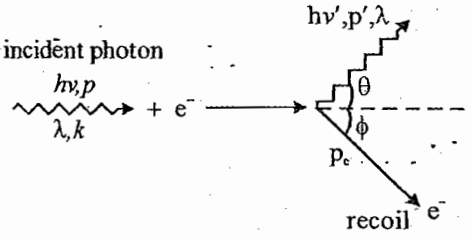
Stoping potential is the potential at which photo current is zero.



Compton effect: In the scattering of electromagnetic theory radiation with the charged particle the wavelength of radiation after scattering is larger than that of incident radiation wavelength.

According to classical mechanics, the radiation emitted should be of same frequency and wavelength as the incident radiation. But it is contradictory to compton effect.

According to Quantum Mechanics we apply Plank's law, $E = nh\nu$ i.e. we take radiation as comprised of particles or quanta of energy $h\nu$ i.e photon.



Applying law of momentum conservation along horizontal direction: $\frac{h}{\lambda} = \frac{h}{\lambda'}\cos\theta + mv\cos\phi$ ... (i)

Applying law of momentum conservation along vertical direction: $0 = \frac{h}{\lambda'}\sin\theta - mv\sin\phi$ ... (ii)

Applying law of conservation of energy: $\frac{hc}{\lambda} = \frac{hc}{\lambda'} + mc^2 - m_e c^2$ ... (iii)

From (i) & (ii) we get, $m^2v^2 = \frac{h^2\nu^2}{c^2} + \frac{h^2\nu'^2}{c^2} - 2\frac{h^2\nu\nu'}{c^2}\cos\theta$ ... (iv)

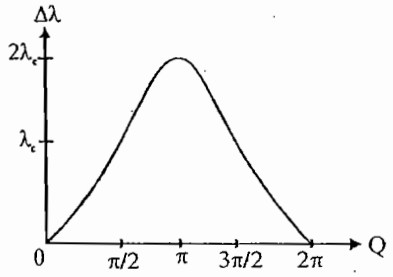
From (iii) we get, $m^2c^2 = \frac{h^2\nu^2}{c^2} + \frac{h^2\nu'^2}{c^2} + m_e^2c^2 - 2\frac{h^2\nu\nu'}{c^2} + 2hm_e(\nu - \nu')$

$$\Rightarrow m^2c^2 - m_e^2c^2 = m^2v^2 = \frac{h^2\nu^2}{c^2} + \frac{h^2\nu'^2}{c^2} - 2\frac{h^2\nu\nu'}{c^2} + 2hm_e(\nu - \nu') \quad \text{... (v)}$$

From (iv) & (v) we get, $2\frac{h^2\nu\nu'}{c^2}(1-\cos\theta)=2hm_e(\nu-\nu')\Rightarrow\Delta\lambda=\lambda'-\bar{\lambda}=\frac{h}{m_ec}(1-\cos\theta)$

This change in wavelength is called as compton shift and depends only on scattering angle and not frequency or wavelength or intensity of the incident radiation.

here, λ_c=compton wavelength=0.02426 A^0



Transfer of energy increases as Q increases.
For bound state wavelength shift is negligible so we say that Compton scattering takes place only for free particles.

Problem: In compton scattering an incoming photon of wavelength $\lambda_0=\frac{3h}{2mc}$, is scattered backward at an angle 180°. The momentum corresponding to recoiling electron is:

(i) $\frac{20}{21}mc$ (ii) $\frac{8}{21}mc$ (iii) $\frac{21}{20}mc$ (iv) $\frac{16}{21}mc$

Soln. $\lambda'-\lambda=\frac{h}{mc}(1-\cos\theta)\Rightarrow\lambda'=\frac{3h}{2mc}+\frac{2h}{mc}=\frac{h}{mc}\left(\frac{2}{3}+2\right)=\frac{7h}{2mc}$

$$\Rightarrow\frac{h}{\lambda}p_e^2=\left(\frac{h}{\lambda}\right)^2+\left(\frac{h}{\lambda'}\right)^2+\frac{2h^2}{\lambda\lambda'}=\frac{h^2}{\lambda\lambda'}\left(\frac{1}{\lambda}+\frac{1}{\lambda'}+2\right)=h^2\left[\frac{1}{\lambda^2}+\frac{1}{\lambda'^2}+\frac{2}{\lambda\lambda'}\right]=h^2\left[\frac{1}{\lambda}+\frac{1}{\lambda'}\right]$$

$$=h^2\left[\frac{1}{\lambda}+\frac{1}{\lambda'}\right]^2$$

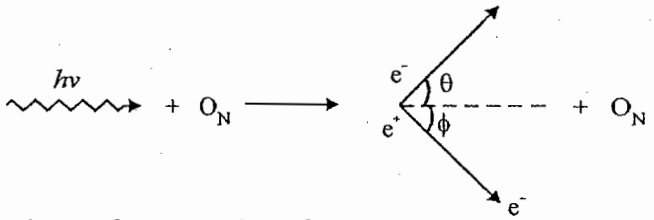
$$\Rightarrow p_e=h\left[\frac{1}{\lambda}+\frac{1}{\lambda'}\right]=\frac{2m_c}{3}+\frac{2m_e}{7}=2m_c\left(\frac{10}{21}\right)=\frac{20\,m_e}{21}$$

So, correct answer is (i)

Pair production:
Conversion of photon in to particle and its antiparticle.

or

Materialisation of radiation or conversion of energy in to mass.



Applying laws of conversation of energy and momentum.

$$h\nu+m_Nc^2\xrightarrow{=}K_N+m_Nc^2+k_{e^-}+k_e+2m_ec^2$$

$$\Rightarrow \quad h\nu = K_N + K_{e^-} + K_{e^+} + 2m_e c^2$$

Minimum energy for pair production $= 2m_e c^2 = 1.022\ MeV$

For free space, $h\nu = 2m_e c^2 + k_{e^-} + k_{e^+} = m_1 c^2 + m_2 c^2$

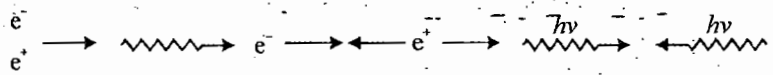
$$= \gamma\, m_{e^-} c^2 + \gamma\, m_{e^+} = 2\gamma\, m_e c^2 \qquad \ldots (1)$$

Momentum conversation, $\frac{h\nu}{c} = 2|p|\cos\theta = 2m_e \cos\theta = 2\gamma m_e c\left(\frac{v}{c}\right)$

$$\Rightarrow \quad h\nu = 2\gamma m_e c^2\left(\frac{v}{c}\right) \qquad \ldots (2)$$

Comparing (1) and (2) we get the condition that if energy is conserved then linear momentum is not conserved. If linear momentum is conserved then energy is not conserved i.e both are not conserved simultaneously. So, pair production don't take place in free space due to non-conservation of energy and linear momentum simultaneously.

Pair anihilation: Inverse of pair production or conversion of mass into energy.



In pair anhilation atleast two photons generates not less than this-more than two photons may be generated but probability of generation of more than two photons is very low because to generate 3 or more than 3 photons very large K.E. is needed to be supplied to the particle and antiparticle.

WAVE ASPECT OF PARTICLES

De-Broglie's Hypothesis: Matter waves $\Rightarrow$ In 1923 de-Broglie thought that this wave particle duality is not restricted to radiation, but, must be universal: all material particles should also display a dual (wave-particle) behaviour. According to de-Broglie a moving particle, whatever its nature, has wave properties associated with it i.e. each material particle of momentum $\vec{p}$ behaves as a group of waves.

de-Broglie wavelength λ associated with any moving particle of momentum p is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \ \& \text{ wave vector } \vec{K} = \frac{\vec{p}}{h}$$

These relations are called de-Broglie relations de Broglie's concept was confirmed experimentally in 1927 by Davison & Germer and later by Thomson, who obtained interference patterns with electrons.

The general rule for the detection of wave-behaviors of any object is:

Whenever the de-Broglie wavelength associated with any object is in the range of or exceeds, its size, the wave nature of this object is detectable. But if its de-Broglie wavelength is too small compared to its size, the wave nature of this object is undetectable.

For understand these things we calculate de-Broglie wavelength for macroscopic and microscopic systems.

Example: Calculate the de-Broglie wavelength for

(a) a proton of kinetic energy 70 MeV Ans. = 3.4×10^{-15} meter

(b) a 10 gm bullet moving at 900 m/sec Ans. = 7.4×10^{-34} m

The wavelength associated with proton has the same order of magnitude as the size of atomic nucleus. The wave aspect of the proton cannot be neglected.

The ratio $\frac{\lambda_b}{\lambda_p} = 2.2\times10^{-19}$ the wave aspect of the bullet lies beyond the human observational abilities.

Problem: Find the de-Broglie wavelength in angstroms for an electron of energy V electron volts (or for an electron accelerated through the potential difference V)

Soln. $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{6.62\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-19}V}}\text{meter} = \frac{12.28\times10^{-10}}{\sqrt{V}} = \frac{12.28}{\sqrt{V}}\ \text{Å} = = \sqrt{\frac{150}{V}}\ \text{Å}$

The non-relativestic de-Broglie wavelength for a proton accelerated through the potential difference V is given by $\lambda = \frac{0.287}{\sqrt{V}}$ Å

The de-Broglie wavelength of a material particle at temperature T is given by

$\lambda = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2mkT}}$ $\Rightarrow$ E = kT Most probable kinetic energy at temperature T

$$= \frac{1}{2}mv_p^2 = \frac{1}{2}m\times\frac{2kT}{m} = kT$$

Problem: Show that the relativestic de-Broglie wavelength associated with a charged particle of charge q accelerated through potential difference V is given by

$$\lambda = \frac{h}{\sqrt{2m_0qV\left(1+\frac{qV}{2m_0c^2}\right)}}$$

Problem: Calculate the de-Broglie wavelength of thermal neutrons at 20°C

Soln. 2Å approximately

Wave Packets :

A superposition of waves or group of waves of slightly different wave-lengths and velocities, with amplitude and phases so chosen that they interfere constructively in small region of space (in neighbourhood of particle) and destructively elsewhere.

A localized wave function is called wave-packet.

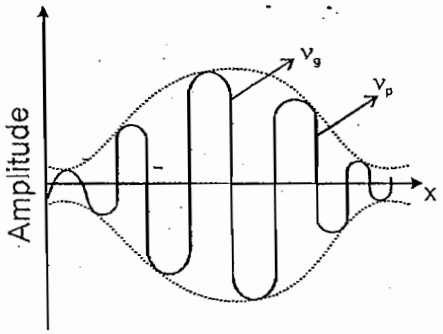
If the wave function is made to vanish every where except in the neighbourhood of particle, it is called localized wavefunction. If the wave function depend on the whole space, it is called non localised.

Not only the wave packets useful in the description of particles that are confined to a certain spatial region, they also play a key role in understanding the connection between classical mechanics and quantum mechanics. The wave-packet embody nature's particle like behaviour and also its wave-like behaviour.

Group velocity and phase velocity :

Phase velocity is the average velocity of individual waves ,forming the packet. The velocity propagation of phase of individual waves that comprises wave packet.

Group velocity represents the velocity with which the wave packet propagates as whole or the velocity of envelope. The velocity of advancement of max amplitude for a group of wave is called group velocity.



Note: The envelope moves with group velocity and individual ripples moves with phase velocity.

The phase velocity and group velocity are defined as $v_p = \frac{\omega}{k}$ & $v_g = \frac{d\omega}{dk}$

Relation between group velocity and phase velocity:

$$v_g = \frac{d\omega}{dk} = \frac{d(v_p k)}{dk} = v_p + k\frac{dv_p}{dk} = v_p + \hbar k\frac{dv_p}{d\hbar k} = v_p + p\frac{dv_p}{dp} \qquad \Rightarrow k = \frac{2\pi}{\lambda}, \quad dk = -\frac{2\pi}{\lambda^2}d\lambda$$

$$\Rightarrow \qquad v_g = v_p - \frac{2\pi}{\lambda}\frac{dv_p}{\frac{2\pi}{\lambda^2}d\lambda} = v_p - \lambda\frac{dv_p}{d\lambda}$$

Group velocity in general may be larger or smaller than the phase velocity depending upon the medium.

For non dispersive medium $\frac{dv_p}{d\lambda} = 0$ (i.e. phase velocity do not depend on the wavelength)

$v_g = v_p$

For dispersive medium $\frac{dv_p}{d\lambda} \neq 0$ (i.e. phase velocity depends upon the wavelength) v_g may be larger and smaller than v_p

For normal dispersive medium, $\frac{dv_p}{d\lambda} = +ve \qquad , v_g < v_p$

For Anomalous dispersive medium, $\frac{dv_p}{d\lambda} = -ve, \qquad v_g > v_p$

Problem: Prove that group velocity of the wave packet is classical velocity of particle.

Soln. $v_g = \frac{d\omega}{dk} = \frac{d(\hbar\omega)}{d(\hbar k)} = \frac{dE}{dp}, \qquad v_p = \frac{\omega}{k} = \frac{E}{p}$

Consider the case of a particle travelling in a constant potential V its total energy is

$$E = \frac{p^2}{2m} + V$$

$$v_g = \frac{dE}{dp} = \frac{p}{m} = v_{particle}$$

This suggests we should view the center of the wave packet as travelling like a classical particle that obeys the laws of classical physics, the centre would then follow the classical trajectory of the particle.

Problem: Show that the phase velocity of a non-relativestic free particle is 1/2 of the group velocity.

Soln. de-Broglie wave associated with particle

$$\lambda = \frac{h}{mv_g} \qquad \text{... (i)}$$

$$E = h\nu = \frac{1}{2}mv_g^2 \Rightarrow \upsilon = \frac{E}{h} = \frac{1}{2}\frac{mv_g^2}{h} \qquad \text{...(ii)}$$

The phase velocity is given by

$$v_p = \upsilon\lambda \qquad \text{... (iii)}$$

$$v_p = \frac{1}{2} \times \frac{mv_g^2}{h} \times \frac{h}{mv_g} = \frac{v_g}{2}$$

Problem: The phase velocity of de-Broglie wave is greater than speed of light.

Soln. $k = \frac{2\pi}{\lambda}$ & $\lambda = \frac{h}{mv_g} \Rightarrow k = \frac{2\pi}{h}mv_g \Rightarrow \omega = 2\pi\nu = 2\pi\frac{E}{h} = 2\pi\frac{mc^2}{h}$

$$\Rightarrow v = \frac{\omega}{k} = \frac{\frac{2\pi mc^2}{h}}{\frac{2\pi mv_g}{h}} \Rightarrow v_p = \frac{c^2}{v_g} \qquad v_g < c$$

$v_p > c$ but v_g is always less than 'c' so de Broglie waves does not violet special theory of relativity.

Exercise:

1. Show that for those waves whose angular frequency ω and wave number k obey the dispersion relation $k^2c^2 = \omega^2 + \text{constant}$ the product of the phase and group velocities is equal to c^2, i.e. $v_p v_g = c^2$, where 'c' is the speed of light.

2. Prove that $v_p = c\sqrt{1 + \left(\frac{mc\lambda}{h}\right)^2}$

   Where λ is the de Broglie wavelength associated with particle of mass m.

3. The angular frequency for a wave propagating inside a waveguide is given in terms of the wave number k and width by $\omega = kc\left[1 - \frac{\pi^2}{b^2k^2}\right]^{-1/2}$. Find the phase and group velocities of the wave.

4. The dispersion relation of a certain wave is $\omega = \sqrt{c^2k^2 + m^2}$
   where ω is the angular frequency, k is the wave vector, c is the velocity of light and m is a constant. The group velocity v of the wave has the following properties.
   (a) $v \to c$ as $k \to 0$ and $v \to c$ as $k \to \infty$

(b) $v \to c$ as $k \to 0$ and $v \to \infty$ as $k \to \infty$

(c) $v \to 0$ as $k \to 0$ and $v \to \infty$ as $k \to \infty$

(d) $v \to 0$ as $k \to 0$ and $v \to c$ as $k \to \infty$

5. The angular frequency of the surface waves in a liquid is given by $\omega = \sqrt{gk + \frac{jk^3}{\rho}}$, where

$g \to$ acceleration due to gravity

$\rho \to$ density of liquid

$T \to$ Surface Tension

Find the phase and group velocities for the limiting cases when the surface waves have (a) very large wavelengths (b) very small wavelengths

$$V_g = \frac{d\omega}{dk} = v_\rho + k\frac{dv_\rho}{dk}$$

(a) $v_g = v_{\rho/2}$ (b) $v_g = \frac{3}{2}v_\rho$

Heisenberg Uncertainty Principle:

According to classical mechanics a moving particle has a definite momentum and occupies a definite position in space and it is possible to determine both its position and momentum simultaneously. If the initial conditions $\vec{r}(0)$ & $\vec{v}_0$ and all forces acting on it are known the position $\vec{r}(t)$ and velocity $\vec{v}(t)$ (future behaviour) are uniquely determined by means of Newton's second law. Thus classical mechanics is completely deterministic.

In quantum mechanics, a particle is described by a group of waves of wave packet, that moves with group velocity. Wavepacket spread over space and particle may be found any where within the wave packet. This implies that position of particle is uncertain with the limits of wave packet. Wave packet has velocity spread and hence there is uncertain about the velocity of momentum of particle. This means it is impossible to know where within the wave packet the particle is and what is its exact velocity or momentum. Thus quantum mechanics is completely indeterministic.

In 1927 Heisenberg proposed a very interesting principle of far reaching importance known as the principle of indeterminancy of uncertainty principle. This principle is a direct consequence of dual nature of matter. In its original form, Heisenberg uncertainty principle states that

If the 'x' component of momentum of a particle is measured with a uncertainty Δp_x then its x positions cannot be measured simultaneously more accurately than $\Delta x = \frac{\hbar}{2\Delta p_x}$; $\Delta x \Delta p_x \geq \frac{\hbar}{2}$

Similarly for other components $\Delta y \Delta p_y \geq \frac{\hbar}{2}$ & $\Delta z \Delta p_z \geq \frac{\hbar}{2}$.

This principle indicates that although it is possible to measure the momentum or position of a particle accurately but it is not possible to measure momentum and position simultaneously to an arbitrary accuracy.

Heisenberg uncertainty principle can be generalize to any pair of complementary or canonically conjugate dynamical variables.

"It is impossible to measure two complementary or canonically conjugate dynamical variables simultaneously to abitrary accuracy".

If ΔE is the uncertainty in determining the energy of the system and Δt is the uncertainty in determining the energy time to which this determination refers. Then $\Delta E \Delta t \geq \frac{\hbar}{2}$

Similary, $\Delta J \Delta\theta \geq \frac{\hbar}{2}$, ΔJ uncertainty in angular momentum and, $\Delta\theta$ uncertainty in angular position perpendicular to the component of any angular momentum measured.

Note: We cannot localize a microscopic particle without giving to it a rather large momentum. We can measure the position without disturbing it.
In quantum mechanics one can not get a definite answer about the position and momentum of a particle, only a probabilistic answer is possible.

Application of uncertainty principle:

The principle of uncertainty explains a large number of facts which could not be explained by classical ideas some of its applications are

1. The non existence of the electron in the nucleus:

Radius of the nucleus of any atom is of the order to 10^{-14}meters , than $\Delta x = 2\times10^{-14}$meters
According to Heisenberg uncertainty principle

$$\Delta x\,\Delta p \geq \frac{\hbar}{2} \text{ or } \Delta x \Delta p \approx \hbar \quad \Rightarrow \Delta x \approx \frac{\hbar}{\Delta q} = \frac{1.054\times10^{-34}}{2\times10^{-15}} = 5.275\times10^{-20} \text{ S.I. unit.}$$

This is the minimum uncertainty in momentum than the momentum of electron must be at least comparble with its magnitude $p \approx \Delta p$

$$\text{The kinetic energy, } T = \frac{p^2}{2m} = \frac{(5.20515)^2\times10^{-40}}{2\times9.1\times10^{-31}} = 1.5289\times10^{-9}\,\text{joule} = 9.7\times10^{7}\,\text{eV} = 97\text{MeV}$$

This means if electron exist inside the nucleus their kinetic energy must be of the order of 97 MeV but experimental observation show that no electron in atom possess energy greater than 4 MeV, clearly the electron do not exist in the nucleus.

2. Radius of Bohr's first orbit:

If the uncertainties in position and momentum in first orbit are Δx and Δp respectively. Then according to Heisenberg uncertainty principle

$$\Delta x \Delta p \approx \hbar \qquad \Rightarrow \Delta p \approx \frac{\hbar}{\Delta x}$$

$$\text{The uncertainty in kinetic energy, } \Delta t = \frac{(\Delta p)^2}{2m} \approx \frac{1}{2m}\frac{\hbar}{(\Delta x)^2}$$

$$\text{The uncertainty in potential energy, } \Delta V = -\frac{ze^2}{\Delta x}$$

$$\text{So that the uncertainty in total energy, } \Delta E = \Delta T + \Delta V = \frac{1}{2m}\frac{\hbar^2}{(\Delta x)^2}\frac{ze^2}{\Delta x}$$

The energy will be minimum if

$$\frac{d(\Delta E)}{d(\Delta x)} = 0 \quad \& \quad \frac{d^2(\Delta E)}{d(\Delta x)^2} = +\text{ve}$$

$$\frac{d(\Delta E)}{d(\Delta q)} = -\frac{1}{m}\frac{\hbar^2}{(\Delta x)^3} + \frac{ze^2}{(\Delta x)^2} = 0$$

$$\Delta x \approx \frac{\hbar^2}{mze^2} \quad \Rightarrow \frac{d^2(\Delta E)}{d(\Delta x)} = +ve$$

So the radius of the first orbit is given by q

Wave function:

According to classical mechanics, the state of a system is specified at any time 't' by two dynamical variables the position $\vec{r}(t)$ and the momentum $\vec{p}(t)$. Any other physical quantity relevant to the system, can be calculated in terms of these two dynamical variables.
Similarly all the information about a quantum mechanical system is confined in the quantity $\psi(r,t)$. known as wave function or state function all the dynamical variables canbe calculated from this.

Physical interpretation:

ψ itself has no physical interpretation only square of its norm $[\psi(r,t)]^2$ has meaning, according to Born's probabilistic interpretation, the square of the norm of $\psi(r,t)$ probability density amplitude

$p(\vec{r},t) = [\psi(\vec{r},t)]^2$ position probability density in state $\psi(\vec{r},t)$

The quantity $[\psi(\vec{r},t)]^2 d^3r$ represents the probability of finding the particle at time t, in a volume element d^3r located between $\vec{r}$ and $\vec{r}+\vec{dr}$; $p(\vec{r},t)d^3r = [\psi(\vec{r},t)]^2 d^3r$

Normalization :

The total probability of finding the system some where in space is equal to unity.

$$\int [\psi(\vec{r},t)]^2 d^3r = 1 \qquad ...(1)$$

A wave function is said to normalised if this satisfy above relation (1)
Every acceptable wave function can be normalized by multiplying it by an appropriate constant.
A wave function is normalised it means ψ must go to zero as $x \to \pm\infty, y \to \pm\infty, z \to \pm\infty$

Note:
Those wavefunction for which position probability density not constant can be normalised by condition $\int \psi^* \psi d\tau = 1$
If position probability density constant, then wavefunction can not be normalized by this condition they normalized by the condition.

$$\int \psi_p^*(r)\psi_{p'}^*(r)d^3r = \delta(p-p')$$

Well behaved wave function or physical acceptable(admissible) wavefunction:

A wave function is said to be physically acceptable if this satisfied following conditions

1. $\psi(\vec{r},t)$ must be finite.

2. $\psi(\vec{r},t)$ must be continuous and single valued.
   Since position probability density can have only one value at particular time and place, and is continuous.

3. $\frac{\partial\psi}{\partial x},\frac{\partial\psi}{\partial y},\frac{\partial\psi}{\partial z}$ must be finite, single valued and continuous
   Since momentum, is continuous single valued and finite.

4. ψ must be square integrable, (i.e. $\int\psi^*\psi d^3r$ must be finite)

Note: If $V\to\infty$ any where than $\frac{\partial\psi}{\partial x},\frac{\partial\psi}{\partial y},\frac{\partial\psi}{\partial z}$ is not continuous

Orthonormality condition:

If a system has two wave function $\psi_i,\&\,\psi_j$ then the condition of orthonormality is defined as

$$\int\psi_i^*\psi_j d\tau=\delta_{ij}$$

If $i=j$ (the wave function is said to be normalisable)

If $i\neq j$ (the wave functions are said to be mutually orthogonal.)

Problem: The wave function of a particle is given as $\psi(x)=\frac{1}{\sqrt{a}}e^{-\frac{|x|}{a}}$

(i) Find the probability of finding the particle $-a<x<+a$.
(ii) Find the value of 'b' so that the probability of finding the particle in the range $-b<x<+b$ is 0.5.

Soln. (i) $\text{Probability}=\int_{-a}^{a}\psi^*\psi dx=\int_{-a}^{a}\frac{1}{a}e^{\frac{2x}{a}}dx+\int_{0}^{a}\frac{1}{a}e^{-\frac{2x}{a}}dx=\frac{1}{a}\left[\frac{e^{\frac{2x}{a}}}{\frac{2}{a}}\right]_{-a}^{0}-\frac{1}{a}\left[\frac{e^{-\frac{2x}{a}}}{\frac{2}{a}}\right]_{0}^{a}$

$$=\frac{1}{2}\left(1-e^{-2}\right)-\frac{1}{2}\left(e^{-2}-1\right)=\frac{1}{2}\left(2-2e^{-2}\right)=1-e^{-2}=1-\frac{1}{e^2}=\frac{e^2-1}{e^2}$$

(ii) $\int_{-b}^{b}\psi^*\psi dx=0.5\Rightarrow\int_{-b}^{b}\frac{1}{a}e^{-\frac{2|x|}{a}}dx=\frac{1}{2}\Rightarrow\frac{1}{a}\times2\times\int_{0}^{b}e^{-\frac{2x}{a}}dx=\frac{1}{2}\Rightarrow\frac{2}{a}\left[\frac{e^{-\frac{2x}{a}}}{-\frac{2}{a}}\right]_{0}^{b}=\frac{1}{2}$

$$\Rightarrow\frac{1}{2}=e^{-2b/a}\Rightarrow e^{2b/a}=2\Rightarrow\frac{2b}{a}=\ell n2\Rightarrow\boxed{b=\frac{a}{2}\ell n\,2}$$

Problem: The wave function of a particle confined in a box of length L is

$$\psi(x)=\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\qquad\text{if } 0<x<L$$
$$=0\qquad\text{if elsewhere}$$

Calculate the probability of finding the particle in the region $0 < x < \frac{L}{2}$

Soln. 1/2

Problem: If the probability that x lies between x & x + dx is p(x)dx = ae^{-ax} dx, where $0 > x > \infty$. $a > 0$. Then the probability that x lies between x_1 and x_2 ($x_2 > x_1$) is

(a) $\left(e^{-ax_1} - e^{-ax_2}\right)$ (b) $a\left(e^{-ax_1} - e^{-ax_2}\right)$

(c) $e^{-ax_2}\left(e^{-ax_1} - e^{-ax_2}\right)$ (d) $e^{-ax_1}\left(e^{-ax_1} - e^{-ax_2}\right)$

Soln. **(a)**

Problem: The wavefunction of the certain particle is $\psi = A\cos^2 x$ if $-\frac{\pi}{2} < x < \frac{\pi}{2}$

(i) Find the value of normalisation constant A

(ii) Find the probability that the particle be found between x = 0, $x = \pi/4$

Soln. (i) $\sqrt{\frac{8}{3\pi}}$ (ii) 0.462

Problem: The normalised state of a free particle is represented by a wavefunction.

$$\psi(x,0) = Ne^{-\frac{x^2}{2a^2} + ik_0 x}$$

Find the normalisation constant

Soln. $N = \frac{1}{a^{1/2}\pi^{1/4}}$

Problem: Consider a one dimensional particle which is confined within the region $0 \le x \le a$ & whole wave function is $\psi(x,t) = \sin\left(\frac{\pi x}{a}\right)e^{-i\omega t}$

Calculate the probability of finding the particle in the interval $\frac{a}{4} \le x \le \frac{3a}{4}$

Note: First calculate normalisation constant and then calculate probability.

$\frac{2+\pi}{2\pi} = 0.82$

Soln. Which among the fallowing functions represent physically acceptable wavefunctions

(i) $3\sin\pi x$, (ii) $4 - |x|$ (iii) $\pm\sqrt{5x}$ (iv) x^2

(i) $3\sin\pi x$, since its and its derivatives are finite, single, continuous everywhere and square integrable.

Note:

4-|x| is continuous but not finite and not square integrable

$\pm\sqrt{5x}$ is not finite, single valued and not square integrable

x^2 is not finite and not square integrable. So, these are not physically acceptable wavefunctions.

Problem: Which of the following wave functions cannot be solutions of Schrodinger's equations (or well behaved) why not ?

(a) $\psi = A\sec x$ (b) $\psi = A\tan x$ (c) $\psi = Ae^{x^2}$ (d) $\psi = Ae^{-x^2}$

Soln. (a), (b) & (c)

Note:

(a) $\psi = A\sec x$

(b) $\psi = A\tan x$ are discontinuous and be come infinite at $x =$ odd multiple of $\frac{\pi}{2}$

(c) $\psi = Ae^{x^2}$ is not finite

Problem: Which of the following functions represent acceptable wavefunction of a particle in the range $-\infty \le x \le \infty$

(a) $\phi(x) = A\tan x \quad A > 0$

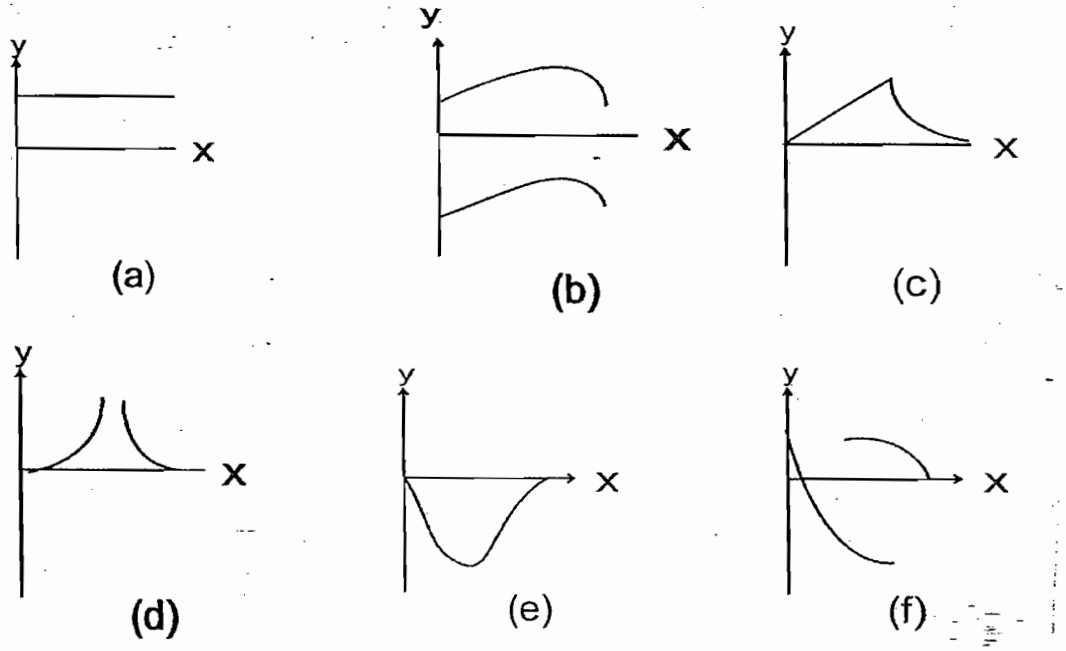
(b) $\phi(x) = B\cos x$, B=constant

(c) $\phi(x) = C\cos\phi e^{-\left(\frac{D}{x^2}\right)}, C > 0, D < 0$

(d) $\phi(x) = E\,x\,e^{-Fx^2}, E > F > 0$

Soln. (d)

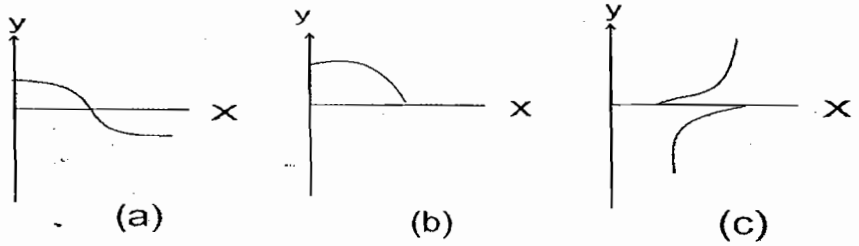
Problem: Which of the wavefunction in figure shown below cannot have physical significance in the interval shown and why not?

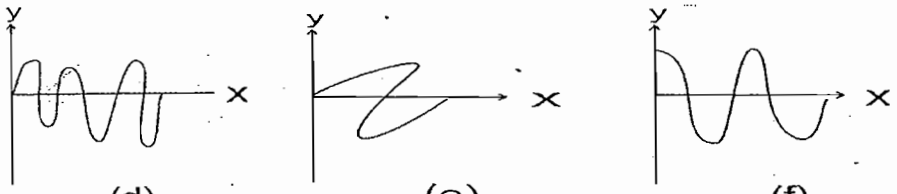


Soln. (b), (c) (d) (f)

Note: since, (b) is double valued (c) has a discontinuous derivative
(d) goes to infinity , ψ discontinuous (f) ψ is discontinuous

Problem: Which of the wave function in figure shown below cannot have physical significance in the interval shown and why not?





(d) (e) (f)

Soln. (c) & (e)

Note: Since, (c) is discontinuous & goes to infinity (e) is not single valued

Fourier Transform:

Wave packet can be constructed by superposing in the same region of space wave of slightly different wavelength but with phases and amplitude so chosen to make the superposition constructive. We can carry out superposition by means of fourier transforms.
For simplicity we consider one dimensional wave packet for instance a particle moving along the x-axis. We can construct the wave packet $\psi(x,t)$ by superposing plane waves (propagate along x-axis) of different frequencies (or wavelength). $\psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\omega t)}dk$ inverse Fourier transform, $\phi(k)$ is the amplitude of wave packet at t=0

$$\psi_0(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{ikx}dk \Rightarrow \phi(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\psi_0(x)e^{-ikx}dx$$ Fourier transfarm

$|\psi_0(x)|$ peaks at x = 0 and vanishes far away from x = 0

as $x\to 0$ we have $e^{ikx}\to 1$ hence the waves of different frequencies interfere constructively on the other hand far away from x = 0 i.e |x|>>0 the phases goes through many periods leading to violant oscillations thereby finding destructive interference

Physical interpretation of the wave packet is obvious:

$\psi_0(x)\to$ probability density amplitude for finding the particle at position x

$|\psi_0(x)|^2\to$ probability density amplitude for finding the particle at position x

$|\psi_0(x)|^2 dx\to$ probability of finding the particle in region between x and x + dx

Note:

(1) The dimension of normalised one-dimension, wavefunction in positions representation

$$=\frac{1}{\sqrt{L}},\left(\text{in2D}.\frac{1}{L}\right),\left(\text{in3D}=\frac{1}{L^{3/2}}\right)$$

(2) The dimension of normalised wavefunction is momentum representation

$$=\frac{1}{\sqrt{P}},\text{in 1-D},\ \frac{1}{P}\text{in 2-D},\frac{1}{P^{3/2}}\text{in 3-D}$$

(3) In wave vector representation $=\frac{1}{\sqrt{K}}$, in 1-D, $\frac{1}{K}$ in 2-D, $\frac{1}{K^{3/2}}$ in 3-D

$$\int_{-\infty}^{\infty}|\psi_0(x)|^2dx=1=\int_{-\infty}^{\infty}|\phi(k)|^2dk$$

If $\psi(x)$ is normalised so is $\phi(k)$ and vice versa.

$|\phi(k)|^2 dk \rightarrow$ probability of finding the particle's wave vector between k and k+dk

we can extract information about the particle's motion by simply expressing its corresponding matter wave in terms of particle energy E and momentum P.

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \phi(p) e^{i(px-Et)\hbar} dp \qquad \Rightarrow \psi_0(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{\frac{ipx}{\hbar}} dp$$

$\phi(p)$ is the momentum amplitude of the packet.

$$\Rightarrow \qquad \phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \psi(x) e^{\frac{-ipx}{\hbar}} dx$$

Problem: Find $\phi(k)$ for a square wave packet $\psi_0(x) = \begin{cases} Ae^{ik_0x} & |x| \le a \\ 0 & |x| > a \end{cases}$

Find the factor A so that $\psi(x)$ is normalised.

Soln. $$\int_{-\infty}^{\infty} (\psi_0(x))^2 dx = |A|^2 \int_{-\infty}^{-a} 0 + \int_{-a}^{a} A^x e^{-ik_0x} A e^{ik_0x} dx + \int_{a}^{\infty} 0$$

$$\Rightarrow 1 = (A)^2 \int_{-a}^{a} dx = (A)^2 2a \Rightarrow (A)^2 = \frac{1}{2a} \Rightarrow (A) = \frac{1}{\sqrt{2a}}$$

$$\Rightarrow \phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi_0(x) e^{-ikx} dx = \frac{1}{2\sqrt{\pi a}} \int_{-a}^{a} e^{ik_0x} e^{-ikx} dx = \frac{1}{2\sqrt{\pi a}} \int_{-a}^{a} e^{i(k_0-k)x} dx$$

$$= \frac{1}{2\sqrt{\pi a}} \frac{e^{i(k_0-k)x}}{ik_0 - k}\Bigg|_{-a}^{a} = \frac{1}{2\sqrt{\pi a}} \left[\frac{e^{i(k_0-k)a} - e^{-i(k_0-k)a}}{i(k_0-k)} \right]$$

$$= \frac{1}{\sqrt{\pi a}} \frac{1}{(k-k_0)} \left[\frac{e^{i(k-k_0)a} - e^{i(k-k_0)a}}{2i} \right] = \frac{1}{\sqrt{\pi a}} \frac{\sin(k-k_0)}{(k-k_0)}$$

Problem: The wave function of a free particle is given by $\psi(x,t) = c\, e^{-\left(x^2+y^2+z^2\right)}$, compute the momentum space probability density and normalisation constant.

$$\left[\psi(p,0)\right]^2 = \frac{(e)^2}{(2\hbar)^3} \exp\left[-\frac{\left(p_x{}^2 + p_y{}^2 + p_z{}^2\right)}{2\hbar^2} \right] \qquad \Rightarrow c = \left(\frac{2}{A}\right)^{3/4}$$

Problem: A quantum mechanical particle in ground state is represented by the wave function $\psi(x) = a^{-1/2}\pi^{-3/4} e^{-x^2/2a^2}$

Find the corresponding momentum wave function $\psi(p) = \frac{\sqrt{a}\pi^{-1/4}}{\hbar} \exp\left(\frac{-px^2q^2}{2\hbar^2} \right)$

UNIT–III

MATHEMATICAL FORMULATION & POSTULATES OF QUANTUM MECHANICS

- **Postulates 1 :** The state of a quantum mechanical system is completely specified by a function $\psi(\bar{r},t)$ (which in general can be complex) that depends on the co-ordinates of the particles (collectively denoted by $\bar{r}$) and on the time. This function, called the **wave function** or the **state function,** has the important property that $\psi^*(\bar{r},t)\ \psi(\bar{r},t)\ d\bar{r}$ is the probability that the system will be found in the volume element $d\bar{r}$, located at $\bar{r}$, at time t.
- **Postulate 2 :** To every observable A in classical mechanics, there corresponds a linear Hermitian operator $\hat{A}$ in quantum mechanics.
- **Postulate 3 :** In any measurement of the observable A, the only values that can be obtained are the eigenvalues a of the associated operator $\hat{A}$, which satisfy the eigenvalue equation $\hat{A}\psi_a = a\psi_a$

  When ψ_a is the eigen function of $\hat{A}$ corresponding to the eigenvalue a.
- **Postulate 4 :** If a system is in a state described by a normalised wave function ψ, and the eigen function $\{\psi a\}$ of $\hat{A}$ are also normalised, then the probability of obtaining the value a in a measurement of the observable A is given by $P(a)=\left|\int_{-\infty}^{\infty}\psi_a^*\psi\, d\bar{r}\right|^2$
- **Postulate 5 :** As a result of a measurement of the observable A in which the value a is obtained, the wave function of the system becomes the corresponding eigen function ψ_a: This is sometimes called the **collapse of the wave function.**
- **Postulate 6 :** Between measurements, the wave function evolves in time according to the time-dependent Schrodinger equation $\frac{d\psi}{dt}=-\frac{i}{h}\hat{H}\psi$

  where $\hat{H}$ is the Hamiltonian operator of the system.

  A hermitian operator $\hat{A}$ is said to be Hermitian if it satisfy the condition.

  In Schriodinger notation $\int\psi_1^*\hat{A}\psi_2\, d\tau = \int(\hat{A}\psi_1)^*\psi_2\, d\tau$ and $\hat{A}=\hat{A}^\dagger$

  In Dirac notation $<\psi_1|\hat{A}\psi_2>=<\hat{A}\psi_1|\psi_2>$ and $\hat{A}=\hat{A}^\dagger$

  The eigenvectors belonging to different eigen values of an observable operator are orthogonal (zero overlap)

  If $\hat{A}|a>=a|a>$

  Then $|a>$ is an eigenvector of the operator $\hat{A}$ with eigenvalue a (which in general is a complex number) The set of all eigenvalues of an operator is called its spectrum, which can take discrete or continuous values (or both) Now let me introduce the well-known 'the commutator concept' The commutator of two operators $\hat{A}$ and $\hat{B}$ is defined as $[\hat{A},\hat{B}]=\hat{A}\hat{B}-\hat{B}\hat{A}$

  In general $\hat{A}\hat{B}\neq\hat{B}\hat{A}$

  Some properties of commutators :

  $[\hat{A},\hat{B}]=-[\hat{B},\hat{A}]$

  $[\hat{A},(\hat{B}+\hat{C})]=[\hat{A},\hat{B}]+[\hat{A},\hat{C}]$

$[\hat{A},\hat{B}\,\hat{C}]=[\hat{A},\hat{B}]\hat{C}+\hat{B}[\hat{A},\hat{C}]$

$[\hat{A},[\hat{B},\hat{C}]]+[\hat{B},[\hat{C},\hat{A},]]+[\hat{C},[\hat{A},\hat{B}]]=0$

$[\hat{A},\hat{B}]^{\dagger}=[\hat{B}^{\dagger},\hat{A}^{\dagger}]$

Let me give some more inputs on operators in qauntum mechanics.

(a) Unit operator, $\hat{1}$: $\hat{1}|a>=|a>$

(b) Zero operator, $\hat{0}$: $\hat{0}|a>=|\text{null}>$

(c) Sum operator, $\hat{A}+\hat{B}$: $(\hat{A}+\hat{B})|a>=\hat{A}|a>+\hat{B}|a>$

(d) Product operator, $\hat{A}\,\hat{B}$: $(\hat{A}\,\hat{B})|a>=\hat{A}(\hat{B}|a>)$

(e) Adjoint operator, $\hat{A}^{\dagger}$:

The adjoint of an operator has the following properties:

$(\alpha\hat{A})^{\dagger}=\alpha\hat{A}^{\dagger}$

$(\hat{A}+\hat{B})^{\dagger}=\hat{A}^{\dagger}+\hat{B}^{\dagger}$

$(\hat{A}\,\hat{B})^{\dagger}=\hat{A}^{\dagger}\hat{B}^{\dagger}$

$(\hat{A}^{\dagger})^{\dagger}=\hat{A}$

If $\hat{A}$ is Hermitian, then $\hat{A}=\hat{A}^{\dagger}$

(f) Unitary operator, $\hat{U}$. The operator $\hat{U}$ is called unitary if $\hat{U}\hat{U}^{\dagger}=\hat{U}^{\dagger}\hat{U}=\hat{1}$

(g) Projection operator, $|a><a|$: Given any normalized vector $|a>$. a projection operator $\hat{P}$ can be defined as the operator that projects any vector into its component along $|a>$

$$\hat{P}|b>=|a><a|b>=(<a|b>)\,|a>\ \hat{P}\rightarrow|a><a|$$

Problem: Prove that $\hat{P}^2=\hat{P}$

Soln. Before a measurement of observable A is made, the system is assumed to be represented by some linear combination (Recall the superposition principle)

$$|\alpha>=\sum_n c_n|n>=\sum_n|n><n|\alpha>$$

When the measurement is performed, the system is thrown into one of the eigenstates, say $|n>$ of observable A. In other words, $|\alpha>\xrightarrow{\text{A measurement}}|n>$

Measurement usually changes the state.

$$|n>\xrightarrow{\text{A measurement}}|n>$$

With certainty, when the measurement causes $|\alpha\rangle$ to change into $|n\rangle$, it is said that A is measured to be n.

As you may relate from already what have been discussed, probability for n, if a system is assumed to be the linear combination.

$$|\alpha\rangle=\sum_n|n\rangle\langle n|\alpha\rangle$$

(a) $|\langle\alpha|n\rangle|$ (b) $|\langle\alpha|n\rangle|^2$ (c) $|\langle n|\alpha\rangle|^2$ (d) $|\langle n|n\rangle|^2$

The answer is already known to you. But still let me give. It is certainly (b).

For the sake of completion let me discuss about two important topics of quantum mechanics, the basis transformation, and the matrix representation of operators.

Basis transformations:

Suppose that $\{|a_n>\}$ and $\{|b_n>\}$ respectively are eigenvectors of the non commuting observables $\hat{A}$ and $\hat{B}$ of a system. This means that we can use either $\{|a_n>\}$ or $\{|b_n>\}$ as basis kets for the Hilbert space. (This is just like representing a vector either by cartesian system of co-ordinates or by spherical polar co-ordinate system according to our convenience). The two bases are related by the transformation.

$|a_n> = \hat{U}|b_n>$ where, $\hat{U} = \sum_i |a_i><b_i|$

Problem: Prove that $\hat{U}$ as defined above is unitary well, let me provide you the proof.

Soln. $\hat{U} = \sum_i |a_i><b_i|$ Clearly, $\hat{U}^\dagger = \sum_i |b_i><a_i|$

Hence, $\hat{U}^\dagger\hat{U} = \sum_i \sum_j |b_i><a_i|a_i|a_j><b_j| = \sum_i |b_i><b_i| = 1 = \hat{1}$. Hence proved.

Problem: Show that the form of the operator equation $\hat{G} = \hat{A}\hat{B}$ preserved under a unitary transformation.

Now, let me talk about the matrix representation of operators in brief (as post graduate students you must have some idea about it)

It is possible to express any operator as $\hat{A} = \hat{1}\hat{A}\hat{1} = \sum_n \sum_{n'} |n'><n'|\hat{A}|n><n|$

where the set $\{|n>\}$ are a set of basis vectors in the Hilbert space and the complex numbers $<n'|\hat{A}|n>$ are a matrix representation of $\hat{A}$. (You should note that the matrix representation of $\hat{A}^\dagger$ is obtained by transposing the matrix representation of $\hat{A}$ and taking the complex conjugate of each element.)

Problem: If $\hat{A}$ is hermitian, then $U = (A + iI)(A - iI)^{-1}$ is

(i) Singular (ii) Anti-hermitian (iii) Symmetric (iv) Unitary

Exercise:

1. If $\sin 2x$ is the eigen function then the eigen value of the operator $\frac{-d^2}{dx^2}$ would be given by

(a) 8 (b) –4 (c) 4 (d) 3.

Soln. **(c)**

2. Two wave function ϕ_1 and ϕ_2 are orthogonal if

(a) $\int \phi_2^* \phi_1 d\tau = 0$ (b) $\int |\phi_2|^2 d\tau = 0$ (c) $\int |\phi|^2 d\tau = 1$ (d) $\int \phi_2^* \phi_1 d\tau = 1$

Soln. **(a)**

Problem: The wave function of a spin less particle of mass 'm' in one dimensional potential is $\psi(x) = A\exp(-\alpha^2 x^2)$ corresponding to an eigen value $E_0 = \frac{\hbar^2\alpha^2}{m}$. The potential V(x) is:

(a) $2E_0(1-\alpha^2x^2)$ (b) $2E_0(1+\alpha^2x^2)$ (c) $2E_0\alpha^2x^2$ (d) $2E_0(1+2\alpha^2x^2)$

Soln. Using time independent schrodinger equation $H\psi = E\psi$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\psi \qquad \ldots(1)$$

$$\psi = A\exp\left(-\alpha^2x^2\right)$$

Wave function depending on position and E will be the eigenvalue then E should be independent of position

Now, $\dfrac{d^2\psi}{dx^2}=\dfrac{d}{dx}\left(\dfrac{d\psi}{dx}\right)=\dfrac{d}{dx}A\exp\left(-\alpha^2x^2\right)\left(-2\alpha^2x\right)$

$$= A\left[\exp\left(-\alpha^2x^2\right)\left(-2\alpha^2x\right)^2+\exp\left(-\alpha^2x^2\right)\left(2\alpha^2\right)\right]$$

$$= 4A\alpha^4x^2\exp\left(-\alpha^2x^2\right)-2\alpha^2A\exp\left(-\alpha^2x^2\right)$$

Equation (1), $-\dfrac{\hbar^2}{2m}\left[4A\alpha^4x^2-2\alpha^2A\right]\exp\left(-\alpha^2x^2\right)+V(x)A\exp\left(-\alpha^2x^2\right)=EA\exp\left(-\alpha^2x^2\right)$

$$-\frac{\hbar^2}{2m}\left[4\alpha^4x^2-2\alpha^2\right]+V(x)=E; \qquad H\psi=E\psi$$

This E is energy eigen value. Then $\hat{H}$ must be position independent as ψ depending on position. Put the position depending part is zero.

$$V(x)-\frac{\hbar^2}{2m}4\alpha^4x^2=0 \qquad \Rightarrow V(x)=2E_0\alpha^2x^2 \qquad \left[\text{as } E_0=\frac{\hbar^2\alpha^2}{m}\right]$$

Correct option is (c).

Problem: A particle of mass 'm' is represented by the wave function $\psi(x)=A\,e^{ikx}$ where 'k' is the wave vector, A is constant. The magnitude of the probability current density of the particle is

(a) $|A|^2\dfrac{\hbar k}{m}$ (b) $|A|^2\dfrac{\hbar k}{2m}$ (c) $|A|^2\dfrac{(\hbar k)^2}{m}$ (d) $|A|^2\dfrac{(\hbar k)^2}{2m}$

Soln. $\psi(x)=A\,e^{ikx} \Rightarrow \psi^*(x)=A^*\,e^{-ikx}$

$$S=-\frac{i\hbar}{2m}\left[\psi^*\nabla\psi-\psi\nabla\psi^*\right]=-\frac{i\hbar}{2m}\left[A^*e^{-ikx}Aik\,e^{-ikx}-A\,e^{ikx}A^*(-ik)e^{-ikx}\right]$$

$$=-\frac{i\hbar}{2m}\left[AA^*ik+AA^*ik\right]=\frac{\hbar k}{2m}\left(2|A|^2\right) \Rightarrow \boxed{S=|A|^2\frac{\hbar k}{m}}$$

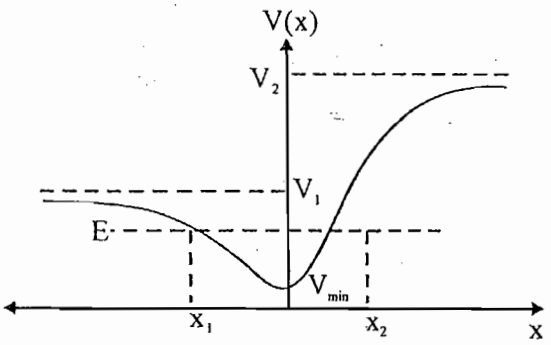
Correct option is (a).

UNIT–IV

BOUND STATES PROBLEM

PROPERTIES OF ONE-DIMENSIONAL MOTION :

To study the dynamic properties of a single particle moving in general one dimensional potential as shown below :



Shape of general potential

$V(x)$ is finite as $x \to \pm\infty$ $\quad \boxed{V(-\infty) = V_1 \quad \& \quad V(+\infty) = V_2 \quad V_1 < V_2}$

(A) **BOUND STATES :** We get bound states if particle is not completely free (i.e. particle can not move to infinity) at the case of Harmonic oscillator, infinite square well, etc. For general potential shown above we get bound states if $V_{min.} < E < V_1$ for this eigen energies or spectrum will be discrete.

For bound states, wavefunctions are finite as $x \to +\infty$ for bound states potential have at least one minimum $V_{min.} < V_1$.

(B) **UNBOUND STATES :** We get unbound state if particle is not confined.

Example: Free particle for potential

$V_1 < E < V_2$ & $E > V_2$ particle is free (unbound states)

(i) $V_1 < E < V_2$ :: For this particle is free to move between $x = x_2$ to $x = -\infty$.

Energy spectrum is continuous & non degenerate. Among two linearly independent solution only one is physically acceptable. The solution that diverge as $x = +\infty$ is not physically acceptable.

(ii) $E > V_2$: Particle is free to move in both directions i.e. motion is infinite in both direction. The energy spectrum is continuous and doubly degenerate.

Note : In contrast to bound states, unbound states cannot be normalised and we cannot use boundary condition.

(i) In a one dimensional problem the energy levels of a bound state system are discrete and non degenerate.

(ii) The wave function of one dimensional bound states system has n nodes if n = 0,

corresponds to ground state and (n-1) nodes (vanishes n-1 times) if n = 1, corresponds to ground state.

FREE PARTICLE : Continuous State

The time independent Schrodinger equation for a particle of mass m, energy E and potential V(x) is:

$$\left[\frac{-\hbar^2\partial^2}{2m\partial x^2}+V(x)\right]\psi(x)=E\psi(x) \qquad \text{... (i)}$$

A free particle is one for which potential energy is quite independent of position and hence for convenience it may be set equal to zero.

The Schrodinger equation for a free particle is given by $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)=E\psi(x)$

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{2mE\psi(x)}{\hbar^2}=0 \qquad \text{... (ii)}$$

$$\frac{\partial^2\psi(x)}{\partial x^2}+k^2\psi(x)=0 \qquad \text{... (iii)}$$

Where $k^2=\frac{2mE}{\hbar^2}$, k is the wave vector

The most general solution of the equation (iii) is

$$\psi(x)=A_+e^{ikx}+A_-e^{-ikx} \qquad \text{... (iv)}$$

$$=\psi_++\psi_- \quad \text{where } A_+ \text{ \& } A_- \text{ are two arbitrary constants.}$$

$$\psi(x,t)=A_+\,e^{i(kx-wt)}+A_-e^{i(kx+wt)}=\psi_+(x,t)+\psi_-(x,t)$$

The first terms represent a wave travelling to the right with intensity $|A_+|^2$ and second term represent a wave travelling to the left with intensity $|A_-|^2$

The probability densities corresponding to either solutions

$$P_\pm(x,t)=|\psi_\pm(x,t)|^2=|A_\pm|^2 \qquad \text{... (v)}$$

are constant, for they do not depend neither on x nor t.

(i) Then according to Heisenberg uncertainty principle, when the momentum and energy of a particle are known exactly $\left(p_\pm=\pm\hbar k, E_\pm=\frac{\hbar^2k^2}{2m}\right)\Delta p=0$ & $\Delta E=0$, there will be total uncertainty about the position and time. A free particle can not have sharply defined momentum and energy

(ii) The speed of the plane waves $\psi_+(x,t)$ is given by :

$$\upsilon_{wave}=\frac{\omega}{k}=\frac{E}{\hbar k}=\frac{\hbar^2k^2}{2m\hbar k}=\frac{p}{2m}$$

$$\upsilon_{classical}=\frac{p}{m}=2\upsilon_p$$

(iii) The wave function is not normalizable

$$\int_{-\infty}^{\infty} \psi_{\pm}^{*} \psi_{\pm} dx = |A_{\pm}|^2 \int_{-\infty}^{\infty} dx \rightarrow \infty$$

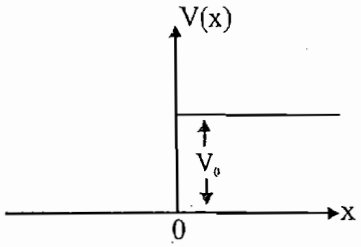
So the free particle is not represented by plane wave or superposition of two linearly independent plane wave but by a wave packet.

THE POTENTIAL STEP :

The function in which potential undergoes only one discontinuous change is called potential step.

The potential step function may be represented as

$$V(x) = \begin{cases} 0 & \text{for } x<0 \\ V_0 & \text{for } x>0 \end{cases}$$

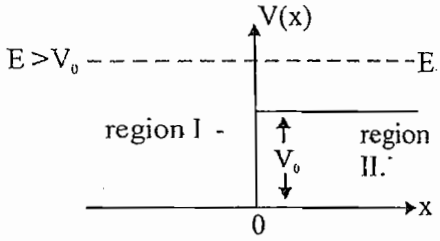


According to classical mechanics if the particle has the total energy $E > V_0$ then particle will always be transmitted and if $E < V_0$ then particle will always be reflected.

But quantum mechanically there is a finite probability of transmission and reflection in both cases.

We treat this problem quantum mechanically.

(i)



The Schrodinger equation is given by $\frac{-\hbar^2}{2m}\nabla^2\psi(x,t) + V(x)\psi(x,t) = E\psi(x,t)$

For first region in one dimension

$$\frac{\partial^2}{\partial x^2}\psi(x) = -\frac{2mE\psi(x)}{\hbar^2}; \qquad \Rightarrow \left(\frac{\partial^2}{\partial x^2} + k_1^2\right)\psi_1(x) = 0 \qquad \text{... (i)}$$

For $x < 0$ (First region), Where $k_1^2 = \frac{2mE}{\hbar^2}$

$$\frac{d^2\psi}{dx^2} = -\frac{2m(E - V_0)}{\hbar^2}\psi(x) \qquad \Longrightarrow \qquad \text{... (ii)}$$

Where $k_2^2 = \frac{2m(E - V_0)}{\hbar^2}$ for $x > 0$ (Second region)

The most general solution to these equations are :

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \quad (x<0) \qquad \text{... (iii)}$$

$$\psi_2(x) = Ce^{ik_2x} + Ce^{-ik_2x} \quad (x>0) \qquad \text{... (iv)}$$

Where, Ae^{ik_1x} → incident wave

Be^{-ik_1x} → reflected wave

Ce^{ik_2x} → transmitted wave

Since there is no probability of reflection for $x > 0$ so, $D = 0$, so, $\psi_2(x) = Ce^{ik_2x}$

$$\psi(x,t) = \begin{cases} \psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}, & x<0 \\ \psi_2(x) = Ce^{ik_2x}, & x>0 \end{cases} \qquad \text{... (v)}$$

Reflection or reflectivity or reflection coefficient is defined as

$$R = \frac{|\text{reflected current density}|}{|\text{incident current density}|} = \frac{|\vec{J}_{\text{ref.}}|}{|\vec{J}_{\text{in.}}|}$$

Transmittance or Transmittivity or transmission coefficient is defined as :

$$T = \frac{|\text{transmitted current density}|}{|\text{incident current density}|} = \frac{|\vec{J}_{\text{trans}}|}{|\vec{J}_{\text{in.}}|}$$

$$\psi_{\text{in.}}^{(x)} = Ae^{ik_1x}, \quad \psi_{\text{ref.}}(x) = Be^{-ik_1x} \quad \psi_{\text{trans.}}(x) = Ce^{ik_2x}$$

$$\vec{J}_{\text{in.}} = \frac{-i\hbar}{2m}\left(\psi_i^*\nabla\psi_i - \psi_i\nabla\psi_i^*\right) = \frac{\hbar k_1}{m}|A|^2$$

$$\vec{J}_{\text{ref.}} = \frac{-i\hbar}{2m}\left(\psi_{\text{ref.}}^*\nabla\psi_{\text{ref.}} - \psi_{\text{ref.}}\nabla\psi_{\text{ref.}}^*\right) = \frac{\hbar k_1}{m}|B|^2$$

$$\vec{J}_{\text{tan.}} = \frac{-i\hbar}{2m}\left[\psi_{\text{trans}}^*\nabla\psi_{\text{trans}} - \psi_{\text{trans}}\nabla\psi_{\text{trans}}^*\right] = \frac{\hbar k_2}{m}|C|^2$$

$$R = \frac{|B|^2}{|A|^2} \qquad T = \frac{k_2|C|^2}{k_1|A|^2} \qquad \text{...(vi)}$$

Boundary conditions are : $\psi_1(0) = \psi_2(0)$ & $\frac{d\psi_1(0)}{dx} = \frac{d\psi_2(0)}{dx}$

On applying boundary condition, we get

$A + B = C$

$k_1(A - B) = k_2C$

$$B = \frac{(k_1 - k_2)}{(k_1 + k_2)}A \qquad C = \frac{2k_1}{(k_1 + k_2)}A$$

$$R = \frac{|k_1 - k_2|^2}{|k_1 + k_2|^2} \qquad T = \frac{|4k_1k_2|^2}{|k_1 + k_2|^2}$$

Since $E > V_0$, k_1 and k_2 are real

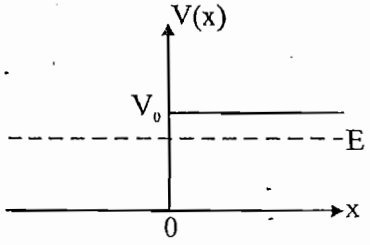
$$R = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} \qquad T = \frac{4k_1k_2}{(k_1 + k_2)^2}$$

$$= \frac{(p_1 - p_2)^2}{(p_1 + p_2)^2} \qquad T = \frac{4p_1p_2}{(p_1 + p_2)^2} \qquad \text{... (vii)}$$

If $V_0 = 0$ $\quad k_1 = k_2$ $\quad R = 0$ $\quad T = 1$
$E = V_0$ $\quad k_2 = 0$ $\quad R = 1$ $\quad T = 0$

It means reflectance will be large if $E \sim V_0$
There must be some reflection if $E >> V_0$.
This does not exist in classical mechanics this is a purely quantum mechanical effect

Case (ii): $E < V_0$



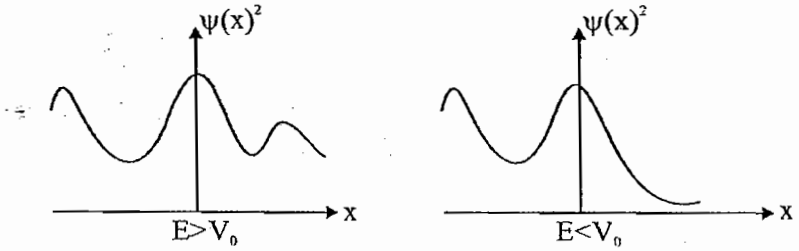
$$\left(\frac{d^2}{dx_2} + k_1^2\right)\psi_1(x) = 0 \qquad x < 0 \qquad \text{(viii)}$$

$$\left(\frac{d^2}{dx^2} + k_2^2\right)\psi_2(x) = 0 \qquad x > 0 \qquad k_2'^2 = \frac{2m(V_0 - E)}{\hbar^2} = -k_2^2$$

$$\psi(x) = \begin{cases} \psi_1(x) = Ae^{ik_1x} + Be^{-ik_2x} \\ \psi_2 = Ce^{ik_2'x} + De^{-ik_2'x} \end{cases} \qquad \text{.... (ix)}$$

D must be zero since otherwise $\psi \to \infty$ as $x \to \infty$ after applying boundary condition we get

$$B = \frac{(k_1 - ik_2')}{(k_1 + ik_2')}A \qquad C = \frac{2k_1}{k_1 + ik_2'}A$$



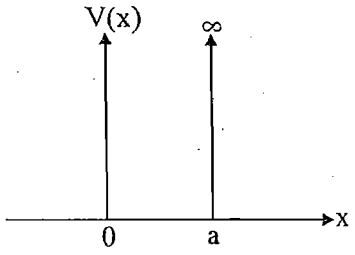
$$R = \frac{|B|^2}{|A|^2} = 1 \qquad T = 0 \qquad \boxed{p_2(x) = |C|^2 e^{-2k_2'x} = \frac{4k_1^2|A|^2}{k_1^2 + k_2'^2}e^{-2k_2'x}}$$

The particle is always reflected as in the classical case. However there is a difference with classical case while none of the particles can be found classically in the region $x > 0$ quantum mechanically there is a non-zero probability that the wave function penetrates this classically forbidden region.

INFINITE SQUARE WELL POTENTIAL :

(i) Unsymmetric square well :

$$V(x) = \begin{cases} +\infty & x < 0 \\ 0 & 0 \le x \le a \\ +\infty & x > a \end{cases}$$



Consider a particle of mass 'm' confined to move inside an infinitely deep unsymmetric potential well defined above.

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \text{where} \quad k^2 = \frac{2mE}{\hbar^2}$$

$$\psi(x) = A'e^{ikx} + B'e^{-ikx} = A\,\text{Sin}kx + B\cos kx$$

Now an applying boundary condition

$$\psi(0) = \psi(a) = 0 \qquad B = 0$$

$$\psi(a) = A\sin ka = 0$$

$$ka = n\pi \qquad n = 1, 2, 3.....$$

$$k = \frac{n\pi}{a} \qquad \boxed{\lambda = \frac{2a}{n}} \qquad \boxed{E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}}$$

Thus energy is quantized. Only certain values are permitted.
'k' have only certain allowed values so, energy is quantized energy spectrum is discrete.
Normalised wavefunction of a particle in infinitely deep square well potential

$$\boxed{\psi_x = \sqrt{\frac{2}{a}}\,\sin\frac{n\pi x}{a}} \qquad n = 1, 2, 3, 4.....$$

$$\boxed{\int \psi_m^* \psi_n dx = \delta mn}$$

$\psi_n(x)$ has (n–1) nodes not taking nodes at $x = 0$, $x = a$.

$\psi_{2n+1}(x)$ are even and $\psi_{2n}(x)$ are odd w.r.t. the centre of the well. None of the energy level is degenerate

$$\psi(x,t) = \sum_{n=1}^{\infty} \psi_n(x) e^{-iE_n t/\hbar}$$

Due to the consequence of uncertainty relation the ground state energy of a particle confined in a well is not zero.

$$\langle x\rangle = \int_{-\infty}^{\infty}\phi_n^* x\phi_n dx = \int_0^L \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)x dx$$

$$< x^2 >= \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} \qquad \Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = L\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}$$

$$\langle p_x\rangle = 0, \langle p_x^2\rangle = n^2\pi^2\frac{\hbar^2}{L^2}$$

$$\Delta p_x = \frac{n\pi\hbar}{L}, \qquad \Delta x\Delta p = n\pi\hbar\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}$$

Problem: Consider a particle of mass m subject to an attractive delta potential $V(x) = -V_0\,\delta(x)$ so where $V_0 > 0$

(a) In the case of negative energies, show that this particle has only one bound state find the binding energy and wave function.

(b) What is the probability that the particles remains bound when V_0 is
(i) Halved suddenly (ii) Quadrupled suddenly.

(c) Study the scattering case (i.e. E > 0) and calculate the reflection and transmission coefficients as a function of the wave number k.

Soln. (a) For bound state case E < 0. The schrodinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2mV_0}{\hbar^2}\delta(x)\psi(x) = \frac{-2mE\psi(x)}{\hbar^2} \qquad ...(i)$$

$$k^2 = \frac{-2mE}{\hbar^2}$$

$$\frac{d^2\psi}{dx^2} + \frac{2mV_0}{\hbar^2}\delta(x)\psi(x) = k^2\psi(x)$$

Since, $\delta(x) = 0$ for $x \neq 0$
$= \infty$ for $x = 0$

The equation for $x \neq 0$

$$\frac{d^2\psi}{dx^2} - k^2\psi(x) = 0 \qquad ...(ii)$$

$$\psi(x) = Ae^{kx} + Be^{-kx} \qquad ...(iii)$$

For bound states as $x \to \pm\infty \quad \psi(x) \to 0$

So, $$\psi(x) = \begin{cases} Ae^{kx} = \psi_-(x), x < 0 & \text{for } -x \Rightarrow B \text{ must be zero to } \psi \text{ vanishes at } x \to -\infty \\ \psi_+(x) = Be^{-kx}, x > 0 & \text{for } +x, A \text{ must be zero to } \psi \text{ vanishes at } x \to \infty \end{cases}$$

Now on applying boundary condition

$\psi_-(0) = \psi_+(0)$ as $\psi(x)$ is continuous at $x = 0 \to A = B$ ...(iv)

Since $V(x) = \infty$ at $x = 0$ so $\frac{d\psi}{dx}$ is not continuous

From Schrodinger equation

$$\int_{-\epsilon}^{\epsilon}\frac{d^2\psi}{dx^2}dx+\frac{2mV_0}{\hbar^2}\int_{-\epsilon}^{\epsilon}\psi(x)\delta(x)dx=-\frac{2mE}{\hbar^2}\int_{-\epsilon}^{\epsilon}\psi x dx\to 0 \quad \text{as } \psi \text{ is continuous at } x=0$$

$$\left.\frac{d\psi}{dx}\right|_{x=+\epsilon}=\left.\frac{d\psi}{dx}\right|_{x=-\epsilon}+\frac{2mV_0A}{\hbar^2}=0 \qquad \text{...(v)}$$

$$\Rightarrow \quad -kA-Bk+\frac{2mV_0A}{\hbar^2}=0$$

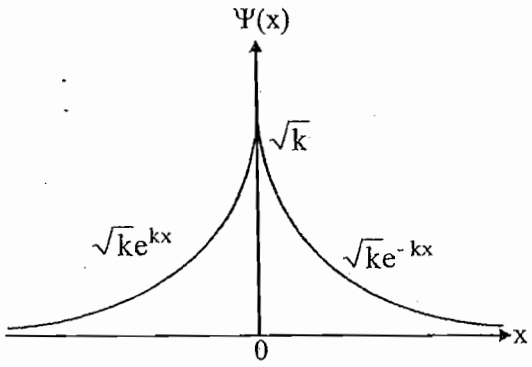
From equation (iv) A = B

$$-2kA+\frac{2mV_0A}{\hbar^2}=0$$

$$k=\frac{mV_0}{\hbar^2}\Rightarrow k^2=\frac{-2mE}{\hbar^2}\Rightarrow\frac{m^2V_0^2}{(\hbar^2)^2}=\frac{-2mE}{\hbar^2}\Rightarrow E=-\frac{m^2V_0^2}{2m\hbar^2} \qquad \text{... (vi)}$$

There is only one bound state.

(b) Normalization condition



Ψ(x)/x

$$\int\psi^*\psi dx=1 \quad \Rightarrow |A|^2\int_{-\infty}^{0}e^{2kx}dx+|A|^2\int_0^{\infty}e^{-2kx}dx=1 \quad \Rightarrow |A|^2\left[2\int_0^{\infty}e^{-2kx}dx\right]=1$$

$$|A|^2\,2\times\left.\frac{e^{-2kx}}{-2\hbar}\right|_0^{\infty}=1 \quad \Rightarrow \quad A=\sqrt{K}$$

$$E=-\frac{mV_0^2}{2\hbar^2} \qquad \text{... (vii)}$$

$$\psi(x)=\sqrt{\frac{mV_0}{\hbar^2}}\,e^{\left(-\sqrt{\frac{mV_0}{\hbar^2}}x\right)} \qquad \text{... (viii)}$$

If the strength of the potential change suddenly from V_0 to V'_0 then probability of finding that the particle remains in bound states :

$$P=|<\psi_1^*|\psi>|^2=\left|\int_{-\infty}^{\infty}\left(\sqrt{\frac{mV'_0}{\hbar^2}}\right)e^{\frac{-mV'_0}{\hbar^2}|x|}\sqrt{\frac{mV_0}{\hbar^2}}e^{-\frac{mV_0}{\hbar^2}|x|}dx\right|^2$$

$$= \left| \frac{m}{\hbar^2}\sqrt{V_0 V'_0} \int_{-\infty}^{\infty} e^{-\frac{m}{\hbar^2}(V_0+V'_0)(x)} dx \right|^2 = \left| \frac{m}{\hbar^2}\sqrt{V_0 V'_0} \left\{ \int_{-\infty}^{0} e^{+\frac{m}{\hbar^2}(V_0+V'_0)x} dx + \int_{0}^{\infty} e^{-\frac{m}{\hbar^2}(V_0+V'_0)x} dx \right\} \right|^2$$

$$= \left| \frac{m}{\hbar^2}\sqrt{V_0 V'_0} \left\{ 2\int_0^{\infty} e^{-\frac{m}{\hbar^2}(V_0+V'_0)x} dx \right\} \right|^2 = \left| \frac{m}{\hbar^2}\sqrt{V_0 V'_0}\, 2 \times \frac{e^{-\frac{m}{\hbar^2}(V_0+V'_0)x}}{-\frac{m}{\hbar^2}(V_0+V'_0)} \right|_0^{\infty} \Bigg|^2$$

$$= \left| \frac{m}{\hbar^2}\sqrt{V_0 V'_0} \times 2 \times \frac{\hbar^2}{m(V_0+V'_0)} \right|^2 = 4\left(\frac{\sqrt{V_0 V'_0}}{V_0 + V'_0} \right)^2 = \boxed{\frac{4V_0 V'_0}{(V_0 + V'_0)^2} = P} \quad \text{... (ix)}$$

(i) If $V'_0 = \frac{V_0}{2}$, the probability of finding the particle in ground states

$$P = \frac{4 \times V_0 \times V_0/_2}{\left(V_0 + \frac{V_0}{2}\right)^2} = \frac{4V_0^2}{9V_0^2} = \frac{8}{9} = 89\%$$

(ii) If $V'_0 = 4V_0$ then $P = \frac{4 \times V_0 \times 4V_0}{(V_0 + 4V_0)^2} = \frac{16V_0^2}{25V_0^2} = \frac{16}{25} = 65\%$

(c) For E > 0 (for scattering states)

$$\frac{d^2\psi}{dx^2} = \frac{-2mE\psi(x)}{\hbar^2} \qquad k^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi}{dx^2} + k^2\psi(x) = 0$$

$\psi(x) = Ae^{ikx} + Be^{-ikx}$ $x < 0$ (Incident and reflected wave) ...(x)

$= Ce^{ikx} + \underset{\Downarrow}{D}e^{-ikx}$ $x > 0$ (Transmitted wave)
0

Now on applying boundary condition :

$$\left(Ae^{ikx} + Be^{ikx}\right)_{x=0} = \left(Ce^{ikx}\right)_{x=0}$$

A + B = C ... (xi)

And from equation (v)

$$\left[\left(\frac{d\psi}{dx}\right)_{x=\epsilon} - \left(\frac{d\psi}{dx}\right)\right]_{x=-\epsilon} + \frac{2mV_0}{\hbar^2}\psi(0) = 0$$

$\epsilon \Rightarrow 0$

$$iAk - ik(A - B) + \frac{2mV_0}{\hbar^2}C = 0 \quad \text{... (xii)}$$

$$ik(A-B)-\left(\frac{2mV_0}{\hbar^2}+ik\right)C=0$$

$$\frac{-\left(ik+\frac{(2mV_0)}{\hbar^2}\right)(A+B)\pm\left(\frac{2mV_0}{\hbar^2}+ik\right)C=0}{ikA-2ikB-ikA-\frac{2mV_0}{\hbar^2}A-\frac{2mV_0}{\hbar^2}B=0}+B\left(\frac{2mV_0}{\hbar^2}+2ik\right)=-2\frac{mV_0}{\hbar^2}A$$

$$\frac{B}{A}=\frac{-2mV_0/\hbar^2}{\left(\frac{2mV_0}{\hbar^2}+2ik\right)}=\left(\frac{-1}{1+\frac{i\hbar^2k}{mV_0}}\right) \quad \text{.... (xiii)}$$

$$ik(A-B)-\left(\frac{2mV_0}{\hbar^2}+ik\right)C=0$$

$$\frac{+ik(A+B)-ikC=0}{+2ikA-\frac{2mV_0}{\hbar^2}C-2ikC=0}\Rightarrow\frac{C}{A}=\frac{2ik}{2ik\left(1-\frac{imV_0}{\hbar^2k}\right)} \quad \text{... (xiv)}$$

$$R=\left|\frac{B}{A}\right|^2 \qquad T=\left|\frac{C^2}{A}\right|$$

$$R=\left(\frac{1}{1+\frac{\hbar^2k^2}{m^2V_0^2}}\right) \quad \& \quad T=\left(\frac{1}{1+\frac{m^2V_0^2}{\hbar^2k^2}}\right) \quad \text{... (xv)}$$

$$R+T=1$$

SYMMETRIC INFINITE POTENTIAL WELL:

$$V(x)=\begin{cases}+\infty, & x\le-\frac{-a}{2}\\ 0, & -\frac{a}{2}<x<+\frac{a}{2}\\ +\infty, & x\ge+\frac{a}{2}\end{cases}$$

$$\psi_n(x)=\sqrt{\frac{2}{a}}\sin\left[\frac{n\pi}{a}\left(x+\frac{a}{2}\right)\right]=\begin{cases}\sqrt{\frac{2}{a}}\cos\frac{n\pi x}{a}, & n=1,3,5,7...\\ \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, & n=2,4,6.....\end{cases}$$

$$\psi = A\sin kx + B\cos kx = A\sin\frac{n\pi x}{a} + B\cos\frac{n\pi}{a}x = A\sin k\frac{a}{2} + B\cos k\frac{a}{2} = 0 - A\sin\frac{a}{2} + B\cos k\frac{a}{2} = 0$$

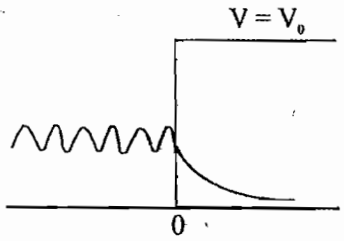
$$B\cos k\frac{a}{2} = 0 \qquad \Rightarrow B = 0 \quad \text{or} \quad \cos\frac{a}{2} = 0 \quad \Rightarrow k\frac{a}{2} = n\frac{a}{2} \Rightarrow k = \frac{n\pi}{a}$$

$n = 1,3,5.....$

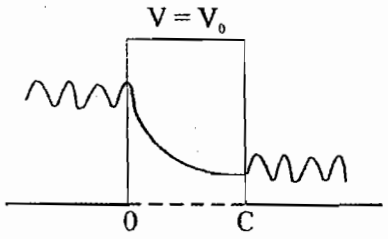
$$A\sin k\frac{a}{2} = 0 \quad \Rightarrow A = 0, \quad \text{or} \quad \sin k\frac{a}{2} = 0 \Rightarrow k\frac{a}{2} = m\pi \qquad \Rightarrow k = \frac{n\pi}{a} \qquad m = 2,4,6.....$$

BARRIER PENETRATION

A particle with energy $E < V_0$ can penetrate a little bit into the classically forbidden region before returning to the allowed region. The typical distance of penetrates, it of the order of $\frac{1}{k_2}$ where $k_2 = \sqrt{2m(V_0 - E)/\hbar^2}$. The wave function decays as $e^{-k_2 x}$ and the probability density $e^{-2k_2 x}$. In a distance of $L = \frac{1}{k_2}$, the probability density will be reduced by $\frac{1}{e^2}$, which is about 10%

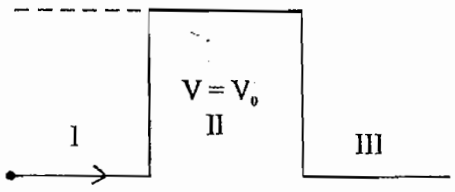


If $V = V_0$ only for a distance L which is smaller than or of the order of $\frac{1}{k_2}$ and again drops to zero. It is not a step potential, it is a barrier



A particle coming from left can penetrate into the classically forbidden region ($V = V_0$) up to a distance L, and if it does so, suddenly it finds V = 0 and this is classically allowed (oscillatory).

Thus if a particle with energy E moves towards a potential barrier with barrier height V_0 which is more than E, there is a finite chance that the potential will appear on the other side of the barrier. This phenomenon is called barrier penetration or tunneling.



$V = 0$ for $x < 0$

$= V_0$ For $0 < x < L$

$= 0$ for $x > L$

rectangular potential barrier

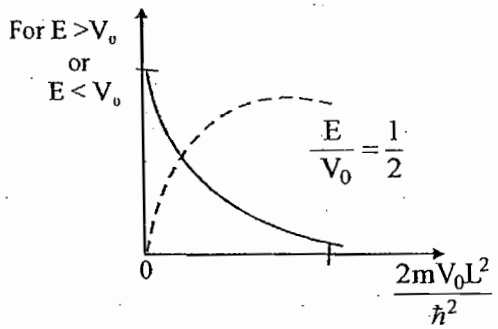
$$\left.\begin{array}{lll} \psi_1 = Ae^{ik_1x} + Be^{-ik_1x} & \text{for} & x < 0 \\ \psi_2 = Ce^{k_2x} + De^{-k_2x} & \text{for} & 0 < x < L \\ \psi_3 = Ee^{ik_3x} & \text{for} & x > L \end{array}\right\} \quad k_1^2 = k_3^2 = \frac{2mE}{\hbar^2}, \quad k_2^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

$$T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2\left\{\sqrt{\frac{2m(V_0 - E)L^2}{\hbar^2}}\right\}} \quad (E < V_0)$$

$$= \frac{4E(E - V_0)}{4E(E - V_0) + V_0^2 \sin^2\left\{\sqrt{\frac{2m(E - V_0)L^2}{\hbar^2}}\right\}} \quad (E > V_0)$$

$$R = \frac{1}{4}\frac{V_0^2 T}{E(V_0 - E)}\sinh^2\left(\sqrt{\frac{2m(V_0 - E)L^2}{\hbar^2}}\right) \qquad (E < V_0)$$

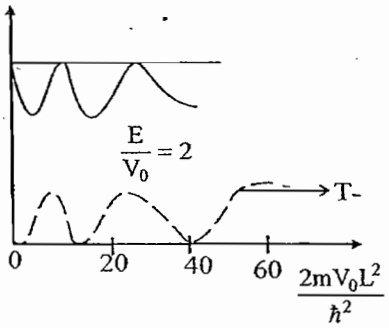
$$= \frac{V_0^2 \sin^2\left(\sqrt{\frac{2m(E - V_0)L^2}{\hbar^2}}\right)}{\sin^2\left(\sqrt{\frac{2m(E - V_0)L^2}{\hbar^2}}\right) + 4E(E - V_0)} \quad (E > V_0)$$



$\sinh k_2 L = i \sin k_2 L \quad (k_2 L << 1)$

As $V_0 L^2$ increases T and R oscillate in manner as shown in figure below.

For certain values of $V_0 L^2$, $T = 1$



Quite often we deal with a situation in which the barrier is quite high as compared to the energy or the barrier width is large or both. The transmittance is then very small for large values of k_2L

$$\sinh k_2L = \frac{e^{k_2L} - e^{-k_2L}}{2} = \frac{e^{k_2L}}{2} \qquad e^{k_2L} >> e^{-k_2L} \qquad \Rightarrow \sinh^2 \frac{k_2L}{2} = \frac{e^{2k_2L}}{4}$$

$$T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sin^2 hk_2L} = \frac{4E(V_0 - E)}{4E(V_0 - E) + \frac{V_0^2 e^{2k_2L}}{4}} \approx \frac{(4E(V_0 - E))}{V_0^2} e^{-2k_2L} \left(\frac{V_0^2}{4} e^{2k_2L} >> 4E \right)$$

Some time e^{-k_2L} is very small and $\frac{16E(V_0 - E)}{V_0^2} \simeq 1 \quad \Rightarrow \boxed{T \simeq e^{-2k_2L} \text{ it } k_2L >> 1}$

(i) α-decay
(ii) Field emission (ejection of electron from metal at relativity low temperature by applying strong electric field near metal)
(iii) Nuclear fusion in sun.
(iv) Tunneling between two metals (scanning tunneling microscope)

Eigenvalues & Eigen functions of energy for a finite square well potential

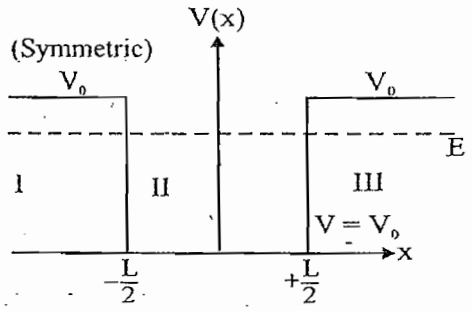
Note: An infinitely deep square well potential keeps the particle bound for any energy that the particle can have. A finite square well potential has a similar shape, but the depth of the well is finite, so it keeps the particle bound for some values not for any energy.

The potential function V(x) for finite square well potential may be written as

$$V(x) = 0 \qquad \text{for} \qquad \frac{-L}{2} < x < \frac{L}{2}$$

$$= V_0 \qquad \text{other wise}$$

Depth of well is V_0 and width is L



Schrodinger equation for first region

$$\frac{d^2\psi_1(x)}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\psi_1(x) = 0 \Rightarrow \frac{d^2\psi_1}{dx^2} - k_2^2\psi_1 = 0 \qquad ...(i)$$

Where, $k_2^2 = \frac{2m(V_0 - E)}{\hbar^2}$

Schrodinger equation for second region,

$$\frac{d^2\psi_2}{dx^2} + \frac{2mE}{\hbar^2}\psi_2(x) = 0 \Rightarrow \frac{d^2\psi_2}{dx^2} + k_1^2\psi_2 = 0 \qquad ...(ii)$$

Where, $k_1^2 = \frac{2mE}{\hbar^2}$

Schrodinger equation for third region,

$$\frac{d^2\psi_3(x)}{dx^2} - \frac{2m(V_0 - E)\psi_3(x)}{\hbar^2} = 0 \Rightarrow \frac{d^2\psi_3(x)}{dx^2} - k_2^2\psi_3(x) = 0 \quad ...(iii)$$

$$\psi_1(x) = Ae^{+k_2x} + Be^{-k_2x}$$

$$\psi_2(x) = C\,e^{ik_1x} + D\,e^{-ik_1x} = C\sin k_1x + D\cos k_1x \qquad ...(iv)$$

$$\psi_3(x) = Ee^{k_2x} + Fe^{-k_2x}$$

For $x < -\frac{L}{2}$ $\psi_1(x)$ should be finite everywhere but at $x = -\infty$, $\psi_1(x) = \infty$

Therefore, B = 0. So, $\psi_1(x) = A\,e^{k_2x}$

For $x > \frac{L}{2}$ $\psi_3(x)$ should be finite everywhere but at $x = \infty$, $\psi_3(x) = \infty$

Therefore, E = 0. So, $\psi_3(x) = F e^{-k_2 x}$

$$\left.\begin{aligned} \psi_1(x) &= Ae^{k_2 x} \\ \psi_2(x) &= C\sin k_1 x + D\cos k_1 x \\ \psi_3(x) &= Fe^{-k_2 x} \end{aligned}\right\} \quad \text{...(v)}$$

EVEN EIGEN FUNCTIONS : For even functions ($C\sin k_1 x$ must be zero as it is odd function)

$$\psi_1(x) = Ae^{k_2 x}, \qquad x < -\frac{L}{2}$$

$$\psi_2(x) = D\cos k_1 x, \qquad -\frac{L}{2} < x < \frac{L}{2}$$

$$\psi_3(x) = Fe^{-k_2 x}, \qquad x > \frac{L}{2} \quad \text{... (vi)}$$

Boundary condition ψ & $\frac{d\psi}{dx}$ must be continuous everywhere.

$$\psi_1(x)\big|_{x=-\frac{L}{2}} = \psi_2(x)\big|_{x=-\frac{L}{2}} \quad \text{... (vii)}$$

$$\left.\frac{d\psi_1}{dx}\right|_{x=-L/2} = \left.\frac{d\psi_2}{dx}\right|_{x=-\frac{L}{2}} \quad \text{... (viii)}$$

$$\psi_2(x)\big|_{x=\frac{L}{2}} = \psi_3(x)\Big|_{x=\frac{L}{2}} \quad \text{... (ix)}$$

$$\left.\frac{d\psi_2}{dx}\right|_{x=L/2} = \left.\frac{d\psi_3}{dx}\right|_{x=L/2} \quad \text{... (x)}$$

Imposing the equation (vii) and (viii), we get

$$Ae^{-\frac{Lk_2}{2}} = D\cos\left(\frac{Lk_1}{2}\right) \text{ and } k_2 Ae^{-\frac{k_2 L}{2}} = Dk_1 \sin\frac{k_1 L}{2} \quad \text{... (xi)}$$

From (xi), we get $k_2 = k_1 \tan\left(\frac{k_1 L}{2}\right)$ ... (xii)

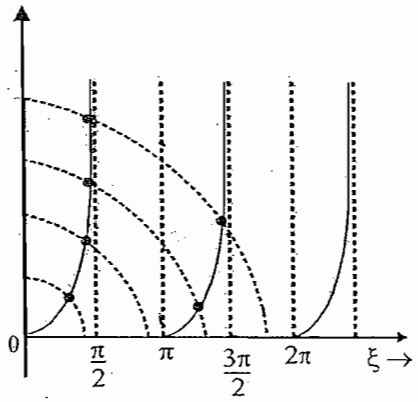
$$\Rightarrow \quad \left(k_2\frac{L}{2}\right) = \left(k_1\frac{L}{2}\right)\tan\left(k_1\frac{L}{2}\right) \qquad \Rightarrow \eta = \xi\tan\xi \quad \text{... (xiii)}$$

Where $\eta = \frac{k_2 L}{2}$ and $\xi = \frac{k_1 L}{2}$

Therefore, $\eta^2 + \xi^2 = \frac{L^2}{4}\left(\frac{2m(V_0 - E)}{\hbar^2} + \frac{2mE}{\hbar^2}\right) = \frac{L^2}{4} \times \frac{2mV_0}{\hbar^2} = \frac{mV_0 L^2}{2\hbar^2}$ ...(xiv)

$\eta^2 + \xi^2$ is constant for a given particle and given potential well.

The posible value of η & ξ can be obtained by using equations (xii) & (xiv). If we plot (xii) & (xiv) with the same axes, the point of intersections give the possible values of energy E.



$\eta^2 + \xi^2 = \dfrac{mV_0L^2}{2\hbar^2} = R^2$; this represents a circle of radius R = $\sqrt{\dfrac{mV_0L^2}{2\hbar^2}}$

Case-I: $0 < R < \pi \quad \Rightarrow 0 < \left(\dfrac{mV_0L^2}{2\hbar^2}\right)^{1/2} < \pi \quad$ as $\Rightarrow \quad 0 < V_0L^2 < \dfrac{2\hbar^2\pi^2}{m}$

There will be only one point of intersection. Therefore, there is only one bound state and one value of energy for even eigen functions.

Case-II: $\pi < R < 2\pi \quad \Rightarrow \dfrac{2\hbar^2\pi^2}{m} < V_0L^2 < \dfrac{8\hbar^2\pi^2}{m}$

There are two point of intersection and thus there will be two values of energy and so, two bound states corresponding to even eigen functions. Similarly for others.

ODD EIGENFUNCTIONS :

For odd eigenfunctions (Dcosk$_1$x must be zero as it is even functions) so we take D = 0)

$$\psi_1(x) = Ae^{k_2x} \quad \text{for} \quad x < -\frac{L}{2}$$

$$\psi_2(x) = C\sin k_1x \quad \text{for} \quad -\frac{L}{2} < x < \frac{L}{2}$$

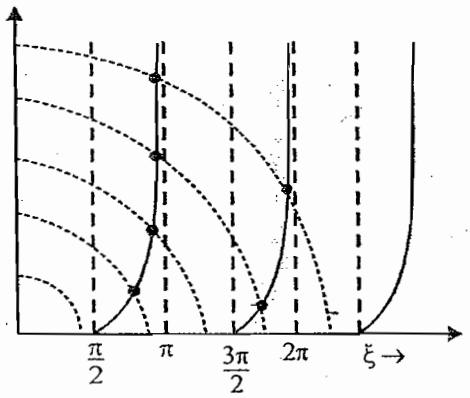
$$\psi_3(x) = Fe^{-k_2x} \quad \text{for} \quad x > \frac{L}{2}$$

On applying boundary conditions

We get $\dfrac{k_2L}{2} = -\dfrac{k_1L}{2}\cot\left(\dfrac{k_1L}{2}\right) \quad \Rightarrow \boxed{\eta = -\xi\cot\xi}$ ...(xii)

$\Rightarrow \boxed{\eta = \xi\tan\left(\dfrac{\pi}{2} + \xi\right)} \quad \Rightarrow \boxed{\eta^2 + \xi^2 = R^2 = \dfrac{mV_0L^2}{2\hbar^2}}$ ... (xiii)

$$\eta^2 + \xi^2 = \frac{mV_0L^2}{2\hbar^2}$$



Case-I: $0 < R < \frac{\pi}{2}$

There is no point of intersection. Therefore, there will be no bound state for odd eigenfunction and no possible value of energy E.

Case-II: $\frac{\pi}{2} < R < 3\frac{\pi}{2} \Rightarrow \frac{\pi^2}{4} < \frac{mV_0L^2}{2\hbar^2} < \frac{9\pi^2}{4} \Rightarrow \frac{\pi^2\hbar^2}{2m} < V_0L^2 < \frac{9\pi^2\hbar^2}{2m}$

There is only one point of intersection. Therefore, there will be one bound state for odd eigenfunction and one possible value of energy E.

R	V_0L^2	Even eigen function	Odd Eigen function	Number of bound states	Odd states	Even states
0 to $\frac{\pi}{2}$	0 to $\frac{\hbar^2\pi^2}{2m}$	1	0	1	0	1
$\frac{\pi}{2}$ to π	$\frac{\hbar^2\pi^2}{2m}$ to $\frac{4\pi^2\hbar^2}{2m}$	1	1	2	1	1
π to $\frac{3\pi}{2}$	$\frac{4\hbar^2\pi^2}{2m}$ to $\frac{9\pi^2\hbar^2}{2m}$	2	1	3	1	2
$\frac{8\pi}{2}$ to 2π	$\frac{9\hbar^2\pi^2}{2m}$ to $\frac{16\pi^2\hbar^2}{2m}$	2	2	4	2	2

Special Features:

1. Finite number of bound states
2. **Barrier penetration:** The phenomenon of particle getting into classically forbidden region is called barrier penetration.

In contrast to infinite number of bound states for an infinite deep potential well there are finite number of bound states for finite well. There is atleast one bound state for even eigenfunction. Existence of other bound states depends on the strength of the potential.

Problem: Show that the ground state energy of a particle of mass m in a finite square well potential of width L is less than that of infinite square well potential.

Soln. Energy eigenvalues in finite square well potential can be obtained by the intersection of the equation $\eta = \xi \tan\xi \;\&\; \eta^2 + \xi^2 = R^2$

For a single bound state to exist

$$\xi < \frac{\pi}{2} \quad \Rightarrow \frac{k_1 L}{2} < \frac{\pi}{2} \quad \Rightarrow \frac{k_1^2 L^2}{4} < \frac{\pi^2}{4} \quad \Rightarrow \frac{2mE}{\hbar^2}\frac{L^2}{4} < \frac{\pi^2}{4} \quad \Rightarrow$$

$$E < \frac{\pi^2 \hbar^2}{2mL^2}$$

Problem: A particle of mass m moves in a potential given by

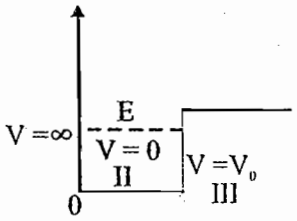
$$\begin{aligned} V(x) &= \infty \quad \text{for} \quad x < 0 \\ &= 0 \quad \text{for} \quad 0 < x < L \\ &= V_0 \quad \text{for} \quad x > L \end{aligned}$$

(a) Write the general form of the stationary state wavefunction in three regions

(b) Applying the boundary conditions, find the transcendental equation satisfied by the energy eigenvalues E

(c) Check that the wavefunctions are the same as the odd solutions in the case of symmetric potential well extended from –L to + L

Soln. **(a)** General eigenfunction



Region I: $\phi_1 = 0$;

Region II: $\phi_2 = A\sin k_1 x + B\cos k_1 x$

Region III: $\phi_3 = Ce^{-k_2 x}$ for $x > L$ where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$ $k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$

(b) $\phi_1(0) = \phi_2(0) \Rightarrow B = 0; \quad \phi_1'(0) = \phi_2'(0)$

$\phi_2(0) = \phi_3(L) \Rightarrow A\sin k_1 L = Ce^{-k_2 L};$

$\phi_2'(L) = \phi_3'(L) \Rightarrow k_1 A\cos k_1 L = -k_1 Ce^{-k_2 L}$

$$k_1 \cot k_1 L = -k_2 \quad \Rightarrow \quad \sqrt{\frac{2mE}{\hbar^2}}\cot\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = -\sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$\phi_1 = 0;\ \phi_2 = A\sin k_1 x;\ \phi_3 = Ce^{-k_2 x}$

Problem: A particle of mass m is confined in the ground state of a one-dimensional box, extending from $x = -2L$ to $+2L$. The wave function of the particle in this state is

$\psi(x) = \psi_0 \cos\left(\frac{\pi x}{4L}\right)$ where ψ_0 is constant.

(i) The normalization factor ψ_0 of this wave function is :

(a) $\sqrt{\frac{2}{L}}$ (b) $\sqrt{\frac{1}{4L}}$ **(c)** $\sqrt{\frac{1}{2L}}$ (d) $\sqrt{\frac{1}{L}}$

(ii) The energy eigenvalue corresponding to this state is :

(a) $\frac{\hbar^2\pi^2}{2mL^2}$ (b) $\frac{\hbar^2\pi^2}{4mL^2}$ (c) $\frac{\hbar^2\pi^2}{16mL^2}$ **(d)** $\frac{\hbar^2\pi^2}{32mL^2}$

(iii) The expectation value of p^2 in this state is

(a) 0 (b) $\frac{\hbar^2\pi^2}{32L^2}$ **(c)** $\frac{\hbar^2\pi^2}{16L^2}$ (d) $\frac{\hbar^2\pi^2}{8L^2}$

Problem: A particle is incident with a constt energy E on a one-dimensional potential barrier as shown in the figure. The wavefunctions in the region I & II are respectively.

(a) Decaying, Oscillatory (b) Oscillatory, Oscillatory
(c) Oscillatory, Decaying (d) Decaying, Decaying

Soln. (c)

Problem: A particle is confined to the region 0<x<L is one dimension. If the particle is in the I[st] excited state, then the probability of finding the particle is maximum at :

(a) $x = L/6$ (b) $x = L/2$ (c) $x = L/3$ (d) $x = \frac{L}{4}$ & $\frac{3L}{4}$

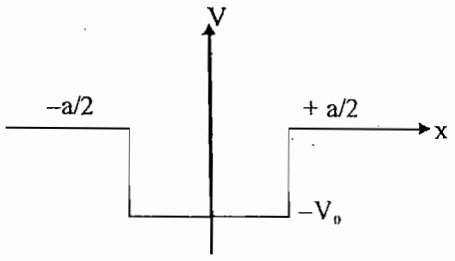
Soln. (d)

Problem: If the particle is in the lowest energy state, then probability of finding the particle in the region $0 < x < \frac{L}{4}$ is :

(a) $\frac{1}{4} - \frac{1}{2\pi}$ (b) $\frac{1}{4}$ (c) $\frac{1}{4} + \frac{1}{2\pi}$ (d) $\frac{1}{2}$

Soln. (c)

Problem: There are only three bound states for a particle of mass m in a one-dimensional potential well of the form shown in the figure.....



The depth of the potential satisfies

(a) $\frac{2\pi^2\hbar^2}{ma^2} < V_0 < \frac{9\pi^2\hbar^2}{2ma^2}$ (b) $\frac{\pi^2\hbar^2}{ma^2} < V_0 < \frac{2\pi^2\hbar^2}{ma^2}$

(c) $\frac{2\pi^2\hbar^2}{ma^2} < V_0 < \frac{8\pi^2\hbar^2}{ma^2}$ (d) $\frac{2\pi^2\hbar^2}{ma^2} < V_0 < \frac{50\pi^2\hbar^2}{ma^2}$

Soln. (a)

Problem: An electron is moving freely inside a one dimensional infinite potential box with walls at x = 0 and x = a. If the electron is initially in the ground state (n = 1) of the box and it we suddenly quadruple the size of the box (x = a to x = 4a).

Calculate the probability of finding the electron is :

(a) The ground state of the new box

(b) The first excited state of the new box

Soln. Initially if the electrons in the ground state of the box x = 0 to x = a

$$E_1 = +\frac{\pi^2\hbar^2}{2ma^2} \qquad \psi_1(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{x\pi x}{a}\right)$$

(a) In new box from x=a to x = 4a the ground state energy & wave function of the electron are :

$$E_1' = +\frac{\pi^2\hbar^2}{32ma^2} \qquad \psi_1'(x) = \frac{1}{\sqrt{2a}}\sin\left(\frac{\pi x}{4a}\right)$$

The probability of finding the electron in $\psi_1(x)$ is :

$$P(E_1') = |<\psi_1'|\psi_1>|^2 = \frac{1}{a^2}\left|\int_0^a \sin\frac{\pi x}{a}\sin\frac{\pi x}{4a}dx\right|^2 = \frac{1}{a^2}\left|\left(\int_0^a \frac{\cos\frac{5}{4}\frac{\pi x}{a}dx - \cos\frac{3\pi x}{4a}dx}{2}\right)\right|^2$$

$$= \frac{1}{a^2}\times\frac{128}{15^2\pi^2}\times a^2 = \frac{128}{15^2\times\pi^2} = 0.058 = 5.8\%$$

(b) In new box from x=a to x = 4a the 1st excited state energy & wave function of the electron are :

$$E_2' = \frac{\pi^2\hbar^2}{8ma^2} \qquad \psi_2'(x) = \frac{1}{\sqrt{2a}}\sin\left(\frac{\pi x}{2a}\right)$$

$$P_2(E_2') = |<\psi_2'|\psi_1>|^2 = \left(\int_0^a \psi_2'^*(x)\psi_1(x)dx\right)^2 = \frac{16}{9\pi^2} = 0.18 = 18\%$$

HARMONIC OSCILLATOR

A particle undergoing simple Harmonic oscillator is called Harmonic Oscillator.
The Hamiltonian of a particle of mass m which oscillates with frequency ω under the influence of a one dimensional Harmonic potential $V(x)=\frac{1}{2}m\omega^2x^2$ is :

$$\hat{H}=\frac{\hat{p}^2}{2m}+\frac{1}{2}k\hat{x}^2=\frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2\hat{x}^2 \qquad \text{where} \quad \omega=\sqrt{\frac{k}{m}}$$

The time independent Schrodinger equation is $-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi+V\psi=E\psi$

in 1-D $$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left(E-\frac{1}{2}kx^2\right)\psi=0 \qquad \text{.... (i)}$$

$$\Rightarrow \qquad \frac{d^2\psi}{dx^2}+2\sqrt{\frac{m}{\hbar^2}}\sqrt{\frac{m}{\hbar^2}}\left(E-\frac{1}{2}kx^2\right)\psi=0 \qquad \Rightarrow$$

$$\frac{d^2\psi}{dx^2}+2\sqrt{\frac{m}{\hbar^2}}\sqrt{\frac{mk}{\hbar^2}}\left(\frac{E}{\sqrt{k}}-\frac{1}{2}\sqrt{k}\,x^2\right)\psi=0$$

$$\Rightarrow \qquad \frac{1}{\sqrt{\frac{mk}{\hbar^2}}}\frac{d^2\psi}{dx^2}+\left[2\sqrt{\frac{m}{k\hbar^2}}E-\sqrt{\frac{mk}{\hbar^2}}x^2\right]\psi=0$$

Now suppose, $\alpha^2=\sqrt{\frac{mk}{\hbar^2}}=\frac{m\omega}{\hbar} \quad \Rightarrow \frac{1}{\alpha^2}\frac{d^2\psi}{dx^2}+\left[\lambda-\alpha^2x^2\right]\psi(x)=0$

$$2\sqrt{\frac{m}{\hbar^2k}}E=\lambda=\frac{2E}{\hbar\omega}$$

Now let $\rho=\alpha x$, $\frac{\partial\rho}{\partial x}=\alpha;\ \frac{\partial\psi}{dx}=\frac{\partial\psi}{\partial\rho}\frac{\partial\rho}{\partial x}=\alpha\frac{\partial\psi}{\partial\rho}$

and $$\frac{\partial^2\psi}{\partial x^2}=\frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\right)=\frac{\partial}{\partial x}\left(\alpha\frac{\partial}{x}\right)=\frac{\partial\psi}{\partial\psi^2}\frac{\partial\rho}{\partial x}=\alpha^2\frac{\partial^2\psi}{\partial x^2}$$

$$\frac{d^2\psi}{d\rho^2}+\left[\lambda-\rho^2\right]\psi=0 \qquad \text{... (ii)}$$

To solve this equation we take assumption that $\rho^2>>\lambda$ and get assymptotic solution

$\psi=e^{\pm\frac{\rho^2}{2}}$, $\quad e^{+\frac{\rho^2}{2}}\to\infty$ as $\rho\to\infty$ so is not physically acceptable

$e^{-\frac{\rho^2}{2}}\to 0$ as $\rho\to\infty$ so it is physically acceptable.

Now let the solution of equation (ii) is :

$$\psi=e^{-\frac{\rho^2}{2}}\phi(\rho) \qquad \text{... (iii)}$$

Now on substituting ψ in (ii) and let

$$\phi(q) = \sum_{r=0}^{\infty} a_r q^{r+s} \qquad \text{... (iv)}$$

And using power sereis method we get

$$\boxed{a_{r+2} = \frac{2s+2r+1-\lambda}{(s+r+2)(s+r+1)} a_r} \qquad \text{recursion formula}$$

$$\text{as } r \to \infty \quad \frac{a_{r+2}}{a_r} = \frac{2}{r} \qquad \text{Behave as } e^{\rho^2}$$

So to make the wave function physically acceptable series (iv) must converge or break off after finite number of terms.

Now suppose that series will break off after nth term then for this

$$2s+2r+1-\lambda = 0$$

$$\lambda = 2s+2r+1$$

for $s+r=n$

$$\lambda = 2n+1 \qquad n = 0,1,2,3.....$$

$$\frac{2E}{\hbar\omega} = \lambda = 2n+1 = 2\left(n+\frac{1}{2}\right) \Rightarrow \boxed{E = \left(n+\frac{1}{2}\right)\hbar\omega}$$

Energy levels of Harmonic Oscillator are equally spaced.

$\phi(\rho) =$ behave as a Hermite polynomial defined as

$$H_n(\rho) = (-1)^n e^{\rho^2} \frac{d^n}{dx^n} e^{-\rho^2}$$

The eigenfunctions of the Linear Harmonic Oscillator is given by

$$\boxed{\psi_n(\rho) = N_n e^{-\frac{\rho^2}{2}} H_n(\rho)}$$

$$\boxed{\psi_n(\rho) = \left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{\rho^2}{2}} H_n(\rho)} \qquad \text{where} \quad \rho = \alpha x$$

$$\int_{-\infty}^{\infty} e^{-\rho^2} H_n(\rho) H_m(\rho) d\rho = 2^n n!\sqrt{\pi}\,\delta_{mn}$$

ANOTHER METHOD:

We can get energy eigenvalues and eigen vectors by using operator method or ladder method.

The Hamiltonian is given by :

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \qquad \text{... (i)}$$

$$\hat{H}=\frac{1}{2}\hbar\omega\left[\frac{\hat{p}^2}{m\hbar\omega}+\frac{m\omega}{\hbar}\hat{x}^2\right]=\frac{1}{2}\hbar\omega\left[\left(\frac{\hat{p}}{\sqrt{m\omega\hbar}}\right)^2+\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x}\right)^2\right]$$

$$\frac{\hat{H}}{\hbar\omega}=\left[\left(\frac{\hat{p}}{\sqrt{2m\omega\hbar}}\right)^2+\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x}\right)^2\right] \quad \text{... (ii)}$$

Now we define two operators

$$\left.\begin{aligned}\hat{a}&=+i\frac{\hat{p}}{\sqrt{2m\omega\hbar}}+\sqrt{\frac{m\omega}{2\hbar}}\hat{x} \quad \text{lowering}\\ \hat{a}^\dagger&=\frac{-i\hat{p}}{\sqrt{2m\omega\hbar}}+\sqrt{\frac{m\omega}{2\hbar}}\hat{x} \quad \text{raising}\end{aligned}\right\}\text{operator} \quad \text{.... (iii)}$$

$$\hat{a}^\dagger\hat{a}=\frac{\hat{p}^2}{2m\omega\hbar}+\frac{m\omega}{2\hbar}\hat{x}^2+\frac{i\hat{x}\hat{p}}{2\hbar}-i\frac{\hat{p}\hat{x}}{2\hbar}=\frac{\hat{p}^2}{2m\hbar\omega}+\frac{m\omega}{2\hbar}\hat{x}^2\frac{+i}{2\hbar}[\hat{x},\hat{p}]=\frac{1}{\hbar\omega}\left[\frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2\hat{x}^2\right]-\frac{1}{2}$$

$$=\frac{\hat{H}}{\hbar\omega}-\frac{1}{2}$$

$$\boxed{\hat{H}=\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)\hbar\omega} \quad \text{... (iv)}$$

$\hat{a}^\dagger\hat{a}$ is called number operator or occuptation number operator.

$$\left[\hat{a},\hat{a}^\dagger\right]=1 \quad \text{... (iii)}$$

$$\left[\hat{a}^\dagger,\hat{a}\right]=-1 \Rightarrow \left[\hat{a}^\dagger\hat{a},\hat{a}\right]=-\hat{a} \quad \& \quad \left[\hat{a}^\dagger\hat{a},\hat{a}^\dagger\right]=\hat{a}^\dagger$$

Energy Eigenvalues :

Since, $\left[\hat{H},\hat{a}\hat{a}^\dagger\right]=\hat{H}\hat{a}\hat{a}^\dagger-\hat{a}\hat{a}^\dagger\hat{H}=\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)\hbar\omega\hat{a}\hat{a}^\dagger-\hat{a}\hat{a}^\dagger\left(\hat{a}\hat{a}^\dagger+\frac{1}{2}\right)\hbar\omega$

$$=\left(\hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger-\hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a}\right)\hbar\omega+\frac{1}{2}\hbar\omega\hat{a}\hat{a}^\dagger-\frac{1}{2}\hbar\omega\hat{a}\hat{a}^\dagger$$

$$=\left[\hat{a}^\dagger\hat{a},\hat{a}\hat{a}^\dagger\right]\hbar\omega$$

$$=\hat{a}\left[\hat{a}^\dagger\hat{a},\hat{a}^\dagger\right]\hbar\omega+\left[\hat{a}^\dagger\hat{a},\hat{a}\right]\hat{a}^\dagger\hbar\omega \quad \text{... (v)}$$

$$=\left(+\hat{a}\hat{a}^\dagger-\hat{a}\hat{a}^\dagger\right)\hbar\omega=0$$

Let $|n\rangle$ be the eigenfunction of $\hat{a}^\dagger\hat{a}$ with eigenvalue n

$$\hat{a}^\dagger\hat{a}|n>=n|n> \quad \text{... (vi)}$$

Since $\hat{H}$ commutes with $\hat{a}^\dagger\hat{a}$ then $|n>$ will also be the eigenfunction it means

$$\hat{H}|n\rangle=\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)\hbar\omega|n\rangle==\left(n+\frac{1}{2}\right)\hbar\omega|n\rangle$$

Then energy eigenvalues are given by :

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega} \qquad \text{... (vii)}$$

$$\left[\hat{a}, \hat{H}\right] = \left[\hat{a}, \left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\hbar\omega\right] = \left[\hat{a}, \hat{a}^\dagger\hat{a}\right]\hbar\omega = \hat{a}^\dagger[a, \hat{a}]\hbar\omega + \left[\hat{a}, \hat{a}^\dagger\right]\hat{a}\hbar\omega = \hbar\omega\hat{a}$$

Similarly, $\left[\hat{a}^\dagger, \hat{H}\right] = -\hbar\omega\hat{a}^\dagger$

Now, $\hat{H}(\hat{a}|n\rangle) = \hat{H}\hat{a}|n\rangle = \left(\hat{a}\hat{H} - \hbar\omega\hat{a}\right)|n\rangle = (\hat{a}E_n - \hbar\omega\hat{a})n >= (E_n - \hbar\omega)\hat{a}|n\rangle$

Similarly $\hat{H}\left(\hat{a}^\dagger|n>\right) = (E_n + \hbar\omega)\hat{a}^\dagger|n>$

$\hat{a}|n>$ & $\hat{a}^\dagger|n\rangle$ are eigenfunctions of $\hat{H}$ with eigenvalue $(E_n - \hbar\omega)$ & $(E_n + \hbar\omega)$ respectively. The action of $\hat{a}$ & $\hat{a}^\dagger$ on $|n>$ generate new energy states that are lower and higher by $\hbar\omega$ respectively. So $\hat{a}$ & $\hat{a}^\dagger$ are called lowering and raising operator or anihilation or creation operator.

Now Let $|n>$ be the eigenfunction of $\hat{a}^\dagger\hat{a}$ with eigenvalue n.

$$\hat{a}^\dagger\hat{a}|n> = n|n>$$

Since $\hat{a}^\dagger\hat{a}$ does not commutes with $\hat{a}^\dagger$ & $\hat{a}$ so $|n>$ is not eigenfunction of $\hat{a}^\dagger$ or $\hat{a}$ or both.

Let, $\hat{a}|n> = C_-|n-1>$ since $\hat{a}$ is lowering operator

$\hat{a}^\dagger|n> = C_+|n+1>$ $\hat{a}^\dagger$ is raising operator

$$<n|\hat{a}^\dagger\hat{a}|n> = <n-1|C_-^*C_-|n-1>$$

$$n<n|n> = |C_-|^2 <n-1|n-1|> \qquad \text{...(viii)}$$

$$|C_-|^2 = (n)^2 = C_- = \pm\sqrt{n}$$

C_- is the norm of $\hat{a}|n>$ and norm can not be negative so, similarly $C_+ = \sqrt{n+1}$

Now matrix element

$$<m|\hat{a}^\dagger\hat{a}|n> = n <m|n> = n\,\delta_{m,n-1}$$

$$<m|\hat{a}|n> = \sqrt{n} <m|n-1> = \sqrt{n}\,\delta_{m,n+1}$$

$$<m|\hat{a}^\dagger|n> = \sqrt{(n+1)} <m|n+1> = \sqrt{(n+1)}\,\delta_{m,n+1}$$

ENERGY EIGENFUNCTIONS :

Using lowering and raising operator we can also find energy eigenfunctions for L.H.O.

$$\hat{a}^\dagger|0> = |1>$$

$$\Rightarrow \quad \hat{a}^\dagger|1> = \sqrt{2}|2> \Rightarrow \frac{\hat{a}^\dagger}{\sqrt{1\times 2}}|1> = |2\rangle \quad \Rightarrow \quad \frac{\left(\hat{a}^\dagger\right)^2}{\sqrt{2!}}|0> = |2\rangle$$

$$\Rightarrow \quad \hat{a}^\dagger|2> = \sqrt{3}|3> \Rightarrow \frac{\hat{a}^\dagger}{\sqrt{3}}|2> = |3\rangle \quad \Rightarrow \quad \frac{\left(\hat{a}^\dagger\right)^3}{\sqrt{3!}}|0> = |3\rangle$$

$$\Rightarrow \quad \hat{a}^\dagger|n-1> = \sqrt{m}|n> \Rightarrow |n\rangle = \frac{\left(\hat{a}^\dagger\right)^n}{\sqrt{n!}}|0>$$

Note: To find any eigenstate n we need simply to operate $\hat{a}^{\dagger}$ on $|0>$, n successive times

(i) Ground state eigen function :

Since n can not be negative

$\hat{a}|0>=0$ since n can not be negative

$<x|\hat{a}|0>=0$

$$\Rightarrow \quad <x\left|\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x}+i\frac{\hat{p}}{\sqrt{2m\omega\hbar}}\right)\right|0>=0$$

$$\Rightarrow \quad <x\left|\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x}+i\frac{\left(-i\hbar\frac{d}{dx}\right)}{\sqrt{2m\omega\hbar}}\right)\right|0>=0 \qquad <x/0>=\psi_0(x)$$

$$\Rightarrow \quad \sqrt{\frac{m\omega}{2\hbar}}\hat{x}\langle x|0\rangle+i\frac{\left(\frac{\hbar}{dx}\right)}{\sqrt{2m\omega}}\frac{d}{dx}\langle x|0\rangle=0 \qquad \Rightarrow \quad \frac{d}{dx}\psi_0(x)=-\frac{m\omega}{\hbar}\hat{x}\psi_0(x)$$

$$\Rightarrow \quad \int\frac{1}{\psi_0(x)}\frac{d\psi_0(x)}{dx}dx=-\frac{m\omega}{\hbar}\int x\times dx \qquad \Rightarrow \quad \log\psi_0(x)=-\frac{m\omega}{2\hbar}x^2-\log A$$

$$\Rightarrow \quad \psi_0(x)=A\exp\left(-\frac{m\omega}{2\hbar}x^2\right)$$

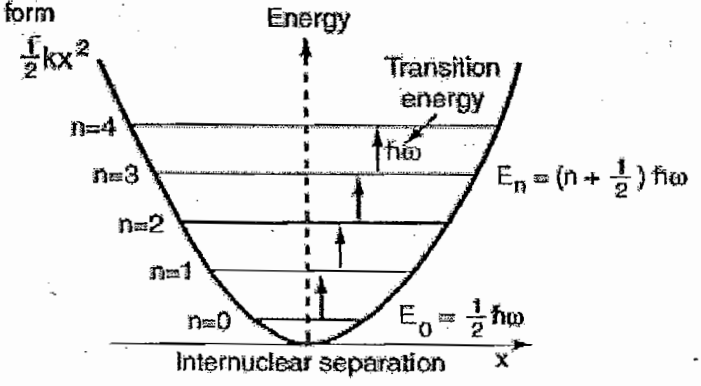
Applying normalization condition: $\int_{-\infty}^{\infty}|\psi_0|^2dx=1 \Rightarrow A=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$

Therefore, the ground state wave fuction will be $\psi_0(x)=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}e^{-\frac{m\omega}{2\hbar}x^2}$

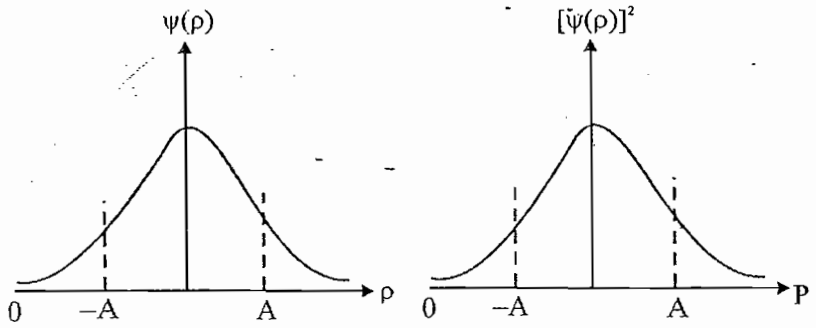
$$\Rightarrow \quad \psi_0(x)=\left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2}e^{-\frac{\alpha^2x^2}{2}} \qquad \text{where } \alpha^2=\frac{m\omega}{\hbar} \qquad \ldots (x)$$

Applying $|n\rangle=\frac{(\hat{a}^{\dagger})^n}{\sqrt{n!}}|0>$, we get $\boxed{\psi_n(x)=\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2}e^{-\rho^2/2}H_n(\rho)}$ where $\rho=\alpha x$

(a) Potential energy of form $\frac{1}{2}kx^2$



(b)



Since $V(-x)=V(x)$ i.e. potential is symmetric parity operator commutes with $\hat{H}$. So every eigenfunction has definite parity.

Harmonic oscillator wavefunction is even for even n and Harmonic oscillator wavefunction is odd for odd n.

Note: From parity considerations it can be deduced immediately that for states of definite parity. The expectation value of any odd operator is always zero without reference to explicit form of ψ.

$$\int\psi^*\hat{x}^n\psi dx \quad = \int\psi^*\hat{p}^n\psi dx \quad = 0 \text{ if n is odd}$$

CORRESPONDENCE PRINCIPLE :

If large values of quantum number, quantum physics yields the same result as classical physics.

$$H_n(y)=(-1)^n e^{y^2}\frac{d}{dx^n}e^{-y^2}$$

$$2yH_n(y)=2nH_{n-1}(y)+H_{n+1}(y)$$

$$H_n'(y)=2nH_{n-1}(y)$$

EXPECTATION VALUES OF VARIOUS OPERATORS :

$$\hat{x}=\sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}+\hat{a}^\dagger\right) \& \hat{p}=\frac{1}{i}\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}-\hat{a}^\dagger\right)$$

$$<n|\hat{x}|n> = \sqrt{\frac{\hbar}{2m\omega}}<n|\left(\hat{a}+\hat{a}^\dagger\right)|n>$$

$$=\sqrt{\frac{\hbar}{2m\omega}}\left[<n|\sqrt{n}|n-1>+<n|\sqrt{(n+1)}|n+1>\right]$$

$$=\sqrt{\frac{\hbar}{2m\omega}}\left[\sqrt{n}<n|n-1>+\sqrt{(n+1)}<n|n+1>\right]=0$$

Similarly, $<n|\hat{p}|n>=0$

$$\langle n|\hat{x}^2|n\rangle = \frac{\hbar}{2m\omega}\langle n|(\hat{a}+\hat{a}^\dagger)^2|n\rangle|$$

$$= \frac{\hbar}{2m\omega}\langle n|(\hat{a}^2+\hat{a}^{\dagger 2}+2\hat{a}^\dagger\hat{a}+1)|n\rangle$$

$$= \frac{\hbar}{2m\omega}\left[\langle n|\sqrt{n}\hat{a}|n-1\rangle + \langle n|\sqrt{(n+1)}\hat{a}^\dagger|n+1\rangle + 2n\langle n|n\rangle + 1\langle n|n\rangle\right]$$

$$= \frac{\hbar}{2m\omega}\left[\sqrt{n}\sqrt{n-1}\langle n|n-2\rangle + \sqrt{(n+1)}\sqrt{(n+2)}\langle n|n+2\rangle + (2n+1)\langle n|n\rangle 0\right]$$

$$= \frac{\hbar}{2m\omega}(2n+1) = \left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}$$

$$\langle n|\hat{p}^2|n\rangle = -\frac{m\hbar\omega}{2}\left[\langle n|(\hat{a}-\hat{a}^+)^2|n\rangle\right] = \left(n+\frac{1}{2}\right)m\hbar\omega$$

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 = \left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega} \qquad \Rightarrow (\Delta p)^2 = \left(n+\frac{1}{2}\right)m\omega\hbar$$

$$(\Delta x)^2(\Delta p)^2 = \left(n+\frac{1}{2}\right)^2\hbar^2 \qquad \Rightarrow \Delta x\Delta p = \left(n+\frac{1}{2}\right)\hbar$$

This is the uncertainty relation for nth eigen state of Linear Harmonic Oscillator

Problem: Let $|0\rangle$ and $|1\rangle$ denote the normalised eigen states corresponding to the ground and first excited state of a 1-dimensional harmonic oscillator. The uncertainity Δp in the state $\frac{1}{\sqrt{2}}(|0\rangle+|1\rangle)$ is:

(a) $\Delta p = \sqrt{\hbar m\omega}/2$ (b) $\Delta p = \sqrt{\hbar m\omega/2}$ (c) $\Delta p = \sqrt{\hbar m\omega}$ (d) $\Delta p = \sqrt{2\hbar m\omega}$

Soln. We know, for odd output $\langle n|\hat{p}|n\rangle = 0$

So, $\langle 0|\hat{p}|0\rangle = 0, \quad \langle 1|\hat{p}|1\rangle = 0,$

$$\langle p\rangle = \langle\psi|\hat{p}|\psi\rangle = \frac{1}{\sqrt{2}}(\langle 0|+\langle 1|)\hat{p}\frac{1}{\sqrt{2}}(|0\rangle+|1\rangle)$$

$$\langle\hat{p}\rangle = \frac{1}{2}\left[\underset{\|}{\langle 0|\hat{p}|0\rangle}_{0} + \langle 0|\hat{p}|1\rangle + \langle 1|\hat{p}|0\rangle + \underset{\|}{\langle 1|\hat{p}|1\rangle}_{0}\right]$$

$$\langle 0|\hat{p}|1\rangle = \left\langle 0\left|\frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}-\hat{a}^\dagger)\right|1\right\rangle = \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}\langle 0|\hat{a}-\hat{a}^\dagger|1\rangle = \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}\left[\langle 0|\hat{a}|1\rangle - \langle 0|\hat{a}^\dagger|1\rangle\right]$$

$$= \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}\left[\underset{\|}{\langle 0|0\rangle}_{1} - \underset{\|}{\langle 0|2\rangle}_{0}\right] \qquad \Rightarrow \langle 0|\hat{p}|1\rangle = \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}$$

$\langle 0|\hat{p}|1\rangle$ & $\langle 1|\hat{p}|0\rangle$ are harmitian conjugate of each other so parallely, $\langle 1|\hat{p}|0\rangle = -\frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}$

Therefore, $\langle \hat{p} \rangle = \langle 0|\hat{p}|1\rangle + \langle 1|\hat{p}|0\rangle = \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}} - \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}} = 0$

$$\langle \hat{p}^2 \rangle = \frac{1}{2}\left[\langle 0|\hat{p}^2|0\rangle + \underbrace{\langle 0|\hat{p}^2|1\rangle}_{0} + \underbrace{\langle 1|\hat{p}^2|0\rangle}_{0} + \langle 1|\hat{p}^2|1\rangle \right]$$

For $\left[\langle n|\hat{p}|n\rangle\right] = \langle m|\hat{p}^2|n\rangle = 0$ [for different m & n (states)]

Since, ψ_1 = odd and ψ_0 = even, integral will be even.

$$\langle 0|\hat{p}^2|0\rangle = \left(n + \frac{1}{2}\right)m\hbar\omega = \frac{1}{2}m\hbar\omega = p_0^2 \text{ and } \langle 1|\hat{p}^2|1\rangle = \left(1 + \frac{1}{2}\right)m\hbar\omega = \frac{3}{2}m\hbar\omega = p_1^2$$

$$\langle \hat{p}^2 \rangle = \frac{1}{2}\times p_0^2 + \frac{1}{2}\times p_1^2 = \frac{1}{2}\times\frac{1}{2}\hbar m\omega + \frac{1}{2}\times\frac{3}{2}\hbar m\omega = \hbar m\omega$$

Therefore, uncertainity in momentum $\Delta p = \sqrt{\langle p^2\rangle - \langle p\rangle^2} = \sqrt{\hbar m\omega - 0} \Rightarrow \boxed{\Delta p = \sqrt{\hbar m\omega}}$

Problem: The energy levels of a particle of mass m in a potential of the form.

$$V(x) = \infty \qquad x \le 0$$
$$= \frac{1}{2}m\omega^2 x^2 \qquad x > 0$$

are given in terms of quantum number n = 0, 1, 2, 3.... by

(a) $\left(n + \frac{1}{2}\right)\hbar\omega$ (b) $\left(2n + \frac{1}{2}\right)\hbar\omega$

(c) $\left(2n + \frac{3}{2}\right)\hbar\omega$ (d) $\left(n + \frac{3}{2}\right)\hbar\omega$

Soln. (c)

3-D PROBLEMS

IN CARTESIAN CO-ORDINATES :

The 3-D time dependent Schrodinger equation for a spinless particle of mass m moving under the influence of a 3-D potential is:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z,t)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z,t)=ih\frac{\partial}{\partial t}\psi(x,y,z,t) \quad ...(i)$$

If potential is independent of time then we can separate time and space part and equation change into time independent Schrodinger equation.

$$\frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z) \quad ...(ii)$$

This partial differential equation is generally difficult to solve. But if potential separates into the sum of three independent, one-dimension terms.

$$V(x,y,z)=V(x)+V(y)+V(z) \quad ...(iii)$$

We can solve Schrodinger's equation by using seperation of variables.

$$\psi(x,y,z)=\psi(x)\psi(y)\psi(z) \quad ...(iv)$$

$\Rightarrow$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)\right]+\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi(y)}{\partial x^2}+V(y)\psi(y)\right]+\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi(z)}{\partial z^2}+V(z)\psi(z)\right]$$

$$=E\psi(x,y,z) \quad ...(v)$$

Right side of equation (v) is constants and in left side each of 3 terms depends on different variables so must be constant.

$$E=E_x+E_y+E_z$$

$$\psi(x,y,z)=\psi(x)\psi(y)\psi(z)$$

PARTICLE IN A THREE DIMENSION BOX :

1. In rectangular box potential or non symmetric box potential. Consider the spinless particle of mass m confined in a rectangular box of sides L_x, L_y, L_z

$$V(x,y,z)=\begin{cases}0 & \text{if } 0<x<L_x, 0<y<L_y, 0<z<L_z\\ \infty & \text{otherwise}\end{cases}$$

$$=V(x)+V(y)+V(z) \quad ... (i)$$

Where, $V(x)=0$ if $0<x<L_x$

$=\infty$ otherwise

$V(y)=0$ if $0<y<L_y$

$=\infty$ otherwise

$V(z)=0$ if $0<z<L_z$

$=\infty$ otherwise ... (ii)

The schrodinger equation for the particle in potential of the form (i)

$$\Rightarrow \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi+\frac{2mE}{\hbar^2}\psi=0 \qquad \Rightarrow \psi(x,y,z)=\psi(x)\psi(y)\psi(z)$$

$$\Rightarrow \frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2}+\frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2}+\frac{1}{\psi(z)}\frac{\partial^2\psi(z)}{\partial z^2}+\frac{2mE}{\hbar^2}=0$$

$$\Rightarrow \frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2}=-\left[\frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2}+\frac{1}{\psi(z)}\frac{\partial^2\psi(z)}{\partial z^2}+\frac{2mE}{\hbar^2}\right] \qquad ...(iii)$$

The right side depends upon z and y and left side on x so must be constant.

$$\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2}=-k_x^2 \Rightarrow \frac{\partial^2\psi(x)}{\partial x^2}+k_x^2\psi(x)=0 \qquad ...(iv)$$

From equation (iii) and (iv), we get

$$\frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2}=k_x^2-\left(\frac{1}{\psi(z)}\frac{\partial^2\psi(z)}{\partial z^2}+\frac{2mE}{\hbar^2}\right) \qquad ...(v)$$

Similarly $\frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2}=-k_x^2 \Rightarrow \frac{\partial^2\psi(y)}{\partial y^2}+k_y^2\psi(y)=0$ ...(vi)

From equation (iii), (iv), (v) and (vi)..

$$\Rightarrow \frac{1}{\psi(z)}\frac{\partial^2\psi(z)}{\partial z^2}=k_x^2+k_y^2-\frac{2mE}{\hbar^2} \qquad ...(vii)$$

$$\Rightarrow \frac{1}{\psi(z)}\frac{\partial^2\psi(z)}{\partial z^2}=-k_z^2 \Rightarrow \frac{\partial^2\psi(z)}{\partial z^2}+k_z^2\psi(z)=0 \qquad ...(viii)$$

$$\Rightarrow \frac{2mE}{\hbar^2}=k_x^2+k_y^2+k_z^2$$

$$\Rightarrow E=\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)=E_x+E_y+E_z \qquad ...(ix)$$

The general solution of (iv), (vi), (viii) are

$$\begin{aligned}\psi(x)&=A\sin k_x x+B\cos k_x x\\ \psi(y)&=C\sin k_y y+D\cos k_y y\\ \psi(z)&=E\sin k_z z+F\cos k_z z\end{aligned} \qquad ...(x)$$

Boundary condition $\Rightarrow$ Wavefunctions must vanish at boundaries i.e.

$$\psi(0)=0=\psi(L_x)=\psi(L_y)=\psi(L_z)$$

We get normalised wavefunction

$$\psi(x,y,z)=\psi(x)\psi(y)\psi(z) \qquad ...(xi)$$

$$=\sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sqrt{\frac{2}{L_z}}\sin\frac{n_x\pi x}{L_x}\sin\frac{n_y\pi y}{L_y}\sin\frac{n_z\pi z}{L_z} \quad (n_x,n_y,n_z=1,2,3.....)$$

Enegy of the particle $E = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right) = E_x + E_y + E_z$ ...(xii)

2. In cubic potential or symmetric box potential :

$V(x,y,z) = 0$ if $0 < x < L, \quad 0 < y < L, \quad 0 < z < L$

$= \infty$ otherwise

From equation (x) & (xi), if $L_x = L_y = L_z = L$

$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x{}^2 + n_y{}^2 + n_z{}^2\right) = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad n_x, n_y, n_z = 1,2,3..... \qquad \text{(xiii)}$$

$$\psi(x,y,z) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right) \qquad \text{(xiv)}$$

For cubic box all the eigenvalues are not non-degenerate they generally degenerate because same $n^2 = n_x^2 + n_y^2 + n_z^2$ can occur for different arrangements of n_x, n_y, n_z. so, $\psi(x,y,z)$ may be different, but E is same.

E	(n_x, n_y, n_z)	Degeneracy (g_n)
3	(111)	1
6	(112),(121),(211)	3
9	(221),(212),(122)	3
11	(311),(131),(113)	3
12	(222)	1
14	(321),(312),(132),(213),(123)	6

Problem: A particle is located in a three dimension cubic well of width L with impenetrable walls. The sum of the energies of the third and fourth level is :

(a) $\frac{10\pi\hbar^2}{mL^2}$ (b) $\frac{10\pi\hbar^2}{3mL^2}$ (c) $\frac{11\pi^2\hbar^2}{2mL^2}$ (d) $\frac{15\pi^2\hbar^2}{2mL^2}$

Soln. (a)

The degeneracy of the forth level is given by :

(a) 1 (b) 2 (c) 3 (d) 4

Soln. (c)

HARMONIC OSCILLATOR :

1. Anisotropic Oscillator :

Consider a particle of mass moving in a three dimensional anisotropic oscillator potential

$$V = \frac{1}{2}m\omega_x^2x^2 + \frac{1}{2}m\omega_y^2y^2 + \frac{1}{2}m\omega_z^2z^2 \qquad \text{... (i)}$$

For this the eigenvalues and eigen functions are

$$E=\left(n_x+\frac{1}{2}\right)\hbar\omega_x+\left(n_y+\frac{1}{2}\right)\hbar\omega_y+\left(n_z+\frac{1}{2}\right)\hbar\omega_z \qquad \text{... (ii)}$$

$$\psi(x,y,z)=\psi_{n_x}(x)\psi_{n_y}(y)\ \psi_{n_z}(x) \qquad \text{...(iii)}$$

where $\psi_n(q)=\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2} e^{-\frac{\alpha^2x^2}{2}} H_n(\alpha q) \qquad \alpha^2=\frac{m\omega}{\hbar}$

$$n\to n_x,n_y,n_z,\ \alpha\to\alpha_x,\alpha_y,\alpha_z,\ q\to x,y,z$$

2. Isotropic Harmonic Oscillator :

3-D Isotropic potential is given by $V=\frac{1}{2}m\omega^2\left(x^2+y^2+z^2\right)$ ...(i)

For isotropic oscillator $\omega_x=\omega_y=\omega_z=\omega$

The eigenvalues

$$En=\left(n_x+\frac{1}{2}+n_y+\frac{1}{2}+n_z+\frac{1}{2}\right)\hbar\omega=\left(n_x+n_y+n_z+\frac{3}{2}\right)\hbar\omega=\left(n+\frac{3}{2}\right)\hbar\omega \quad \text{.... (ii)}$$

where $n=n_x+n_y+n_z\ (n_x,n_y,n_z=0,1,2,3.....)$

$$\psi=\left(\frac{\alpha}{2^{n_x}n_x!\sqrt{\pi}}\right)^{1/2}\left(\frac{\alpha}{2^{n_y}n_y!\sqrt{\pi}}\right)^{1/2}\left(\frac{\alpha}{2^{n_z}n_z!\sqrt{\pi}}\right)^{1/2} e^{-\alpha^2\frac{\left(x^2+y^2+z^2\right)}{2}} H_{n_x}(\alpha x)H_{n_y}(\alpha y)H_{n_z}(\alpha z)$$

... (iii)

For a 3-D isotropic harmonic oscillator the energy eigenvalues are degenerate except ground state as for a given n, n_x, n_y may be different such that $n=n_x+n_y+n_z$ and degeneracy is given by

$$\boxed{g_n=\frac{1}{2}(n+1)(n+2)}$$

n	En	$(n_xn_yn_z)$	g_n
0	$\frac{3}{2}\hbar\omega$	(0,0,0)	1
1	$\frac{5}{2}\hbar\omega$	(100)(001)(010)	3
2	$\frac{7}{2}\hbar\omega$	(110)(011)(101) (200)(020)(002)	6
3	$\frac{9}{2}\hbar\omega$		10

Problem: The degeneracy of the n=2 level for a three dimensional isotropic oscillator is :

(a)4 (b)6 (c)8 (d)10

Soln. (b)

Problem: Consider a spinless particle of mass m which is moving in a three dimension potential

$$V(x,y,z) = \begin{cases} \frac{1}{2}m\omega^2 z^2 & 0<x<a,\ 0<y<b \\ \infty & \text{otherwise} \end{cases}$$

(a) Write down the total energy and the total wave function of the particle

(b) Assuming that $\hbar\omega > \frac{5\pi^2\hbar^2}{ma^2}$. Find the energies and the corresponding degeneracies for the ground state and first excited state.

(c) Assume now that, in addition to the potential $V(x,y,z)$, this particle also has a negative electric charge (–q) and that it is subjected to a constant electric field $\in$ directed along z-axes.

The Hamiltonian along the z-axis is thus given by :

$$\hat{H}z = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + \frac{1}{2}m\omega^2 z^2 - q \in z$$

Derive the expression En_z for this particle and also its total energy En_x, n_y, n_z. Then find the energies and the corresponding degeneracies for the ground state and first excited state.

Soln. (a) $V(x,y,z) = V(x) + V(y) + V(z) = 0$

$V(x) = \text{constant} = V(y) \Rightarrow \text{inf inite potential well}$

$V(z) \Rightarrow \text{Harmonic oscillator along } z-\text{axis}$

Total energy is given by :

$$P = |\langle \psi_0' \mid \psi_0 \rangle|^2 \qquad \text{...(i)}$$

And wave function

$$\psi = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x \pi x}{a}\right)\sqrt{\frac{2}{b}}\sin\left(\frac{n_y \pi y}{b}\right)\psi_{n_z}(z) \qquad \text{...(ii)}$$

where, $\psi_{n_z}(z) = \left(\frac{\alpha}{2^{n_z} n_z! \sqrt{\pi}}\right)^{1/2} e^{\frac{\alpha^2 z^2}{2}} H_{n_z}(\alpha z)$

(b) The energy of the ground state is given by if, a = b will be $E_{110} = \frac{\pi^2\hbar^2}{ma^2} + \frac{\hbar\omega}{2}$

First excited energy :

$$\text{Option 1} : E_{120} = E_{210} = \frac{5\pi^2\hbar^2}{2ma^2} + \frac{\hbar\omega}{2} = \frac{5}{2}\left(\frac{5\pi^2\hbar^2}{ma^2} + \hbar\omega\right)$$

$$\text{Option 2} : E_{111} = \frac{\pi^2\hbar^2}{ma^2} + \frac{3}{2}\hbar\omega = \frac{\pi^2\hbar^2}{ma^2} + \hbar\omega + \frac{\hbar\omega}{2}$$

Since, $\hbar\omega > \frac{5\pi^2\hbar^2}{ma^2}$ $E_{111} > E_{210}$

The first excited state is E_{210} and two fold degenerate.

(c) $\hat{H}_z = \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + \frac{1}{2}m\omega^2 z^2 - q \in z$

Let $z' = z - \frac{q \in}{m\omega^2}$ $dz' = dz$ $\Rightarrow \hat{H}_z = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z'^2} + \frac{1}{2}m\omega^2 z'^2 - \frac{q^2 \in^2}{2m\omega^2}$

$$E_{n_z} = < n_z | H_z | n_z > = \hbar\omega\left(n_z + \frac{1}{2}\right) - \frac{q^2 \in^2}{2m\omega^2}$$

$$E_n = E_{n_x, n_y} + E_{n_z} = \frac{\hbar^2\pi^2}{2ma^2}\left(n_x^2 + n_y^2\right) + \left(n_z + \frac{1}{2}\right)\hbar\omega - \frac{q^2 \in^2}{2m\omega^2}$$

$$E_{110} = \frac{\hbar^2\pi^2}{ma^2} + \frac{1}{2}\hbar\omega - \frac{q^2 \in^2}{2m\omega^2}$$

$$E_{210} = E_{120} = \frac{5\pi^2\hbar^2}{ma^2} + \frac{3n\omega}{2} - \frac{q^2 \in^2}{2m\omega^2}$$

Problem: A particle of mass m and charge q oscillates in a one dimensional Harmonic potential with an angular frequency ω in an electric field $\vec{E} = E_0\hat{x}$. Find the energy eigenvalue of the potential

Soln. Potential energy of the system $= \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$

Potential energy due to electric field $= qE_0x$

Total potential is $V(x) = \frac{1}{2}m\omega^2x^2 + qE_0x$ ... (i)

Schrodinger equation, $\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} = \left[E - \frac{1}{2}m\omega^2x^2 - qE_0x\right]\psi(x) = 0$

$$\Rightarrow \frac{-1}{2}m\omega^2x^2 - qE_0x = -\frac{1}{2}m\omega^2\left[x^2 + \frac{2qE_0}{m\omega^2}\right] = -\frac{1}{2}m\omega^2\left[x^2 + \frac{2qE_0x}{m\omega^2} + \left(\frac{qE_0}{m\omega^2}\right)^2 - \left(\frac{qE_0}{m\omega^2}\right)^2\right]$$

$$= -\frac{1}{2}m\omega^2\left[\left(x + \frac{qE_0}{m\omega^2}\right)^2 - \left(\frac{qE_0}{m\omega^2}\right)^2\right]$$

$$\Rightarrow \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}m\omega^2\left(x + \frac{qE_0}{m\omega^2}\right)^2 + \frac{1}{2}\frac{q^2E_0^2}{m\omega^2}\right]\psi(x) = 0$$

Let $x + \frac{qE_0}{m\omega^2} = x_1$ $E + \frac{1}{2}\frac{q^2E_0^2}{m\omega^2} = E_1$

$$\Rightarrow \quad \frac{-d^2\psi(x)}{dx_1^2}+\frac{2m}{\hbar^2}\left[E_1-\frac{1}{2}m\omega^2x_1^2\right]\psi(x_1)=0 \qquad \text{... (ii)}$$

On comparing with

$$\Rightarrow \quad \frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left[E-\frac{1}{2}m\omega^2x^2\right]\psi(x)=0$$

We get, $E_1=\left(n+\frac{1}{2}\right)\hbar\omega \qquad \Rightarrow E+\frac{1}{2}\frac{q^2E_0^2}{m\omega^2}=\left(n+\frac{1}{2}\right)\hbar\omega \Rightarrow \boxed{E=\left(n+\frac{1}{2}\right)\hbar\omega-\frac{q^2E_0^2}{2m\omega^2}}$

Problem: A particle is initially in the ground state in 1-D Harmonic oscillator, potential $V(x)=\frac{1}{2}kx^2$ If the spring constant is suddenly doubled, calculate the probability of finding the particle in the ground state of the new potential.

Soln. $k'=2k$

$$\Rightarrow \quad \omega=\sqrt{\frac{k}{m}} \qquad \omega'=\sqrt{\frac{k'}{m}}=\sqrt{\frac{2k}{m}}=\sqrt{2}\omega \qquad \Rightarrow \alpha^2=\frac{m\omega}{\hbar}, \qquad (\alpha')^2=\frac{\sqrt{2}\omega m}{\hbar}=\sqrt{2}\alpha^2$$

$$\Rightarrow \quad \psi_n(x)=\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2}e^{-\frac{\alpha^2x^2}{2}}H_n(\alpha x) \qquad \Rightarrow$$

$$\psi_n'(x)=\left(\frac{\alpha'}{2^n n!\sqrt{\pi}}\right)^{1/2}e^{-\frac{\alpha'^2x^2}{2}}H_n(\alpha' x)$$

Required Probability = $P=|<\psi_0'|\psi_0>|^2$

$$<\psi_0'|\psi_0>=\int_{-\infty}^{\infty}\left(\frac{\alpha'}{\sqrt{\pi}}\right)^{1/2}\left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2}e^{-\frac{(\alpha^2+\alpha'^2)}{2}x^2}dx$$

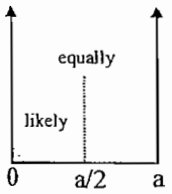
$$=2\left(\frac{\alpha'}{\sqrt{\pi}}\right)^{1/2}\left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2}\int_0^{\infty}e^{-\left(\frac{\alpha^2+\alpha'^2}{2}\right)x^2}dx=\left(\frac{\alpha'}{\sqrt{\pi}}\right)^{1/2}\left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2}\sqrt{\pi}\left(\frac{2}{\alpha^2+\alpha'^2}\right)^{1/2}$$

$$=\frac{2^{\frac{1}{2}}\alpha^{\frac{1}{2}}\alpha'^{\frac{1}{2}}}{\left(\frac{m\omega}{\hbar}+\frac{\sqrt{2}m\omega}{\hbar}\right)^{\frac{1}{2}}}=\frac{2^{1/2}\left(\frac{m\omega}{\hbar}\right)^{1/4}\left(\frac{\sqrt{2}m\omega}{\hbar}\right)^{1/4}}{\left(\frac{m\omega}{\hbar}\right)^{1/2}(1+\sqrt{2})^{1/2}}=\frac{2^{\frac{5}{8}}}{(1+\sqrt{2})^{\frac{1}{2}}}$$

$$\Rightarrow P=\frac{2^{\frac{5}{4}}}{(1+\sqrt{2})}$$

Problem: A particle of mass m in the infinite square well of width a starts out in the left half of the well and is equally likely to be found in that region. Find out, what is the probability of finding the particle in ground state.

Soln. Because of the probability density in the left half region is constant.



Using normalization constant.

$$\int_0^{a/2}|\psi|^2\,dx = 1 \qquad \Rightarrow |A|^2 \times \frac{a}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{a}}$$

$$\phi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \quad \text{for} \quad \text{well of width } a/2$$

$$\psi(x) = C_1\phi_1(x) + C_2\phi_2(x) + \ldots\ldots C_n\phi_n(x) + \ldots..$$

For ground state probability we find C_1

$$C_1 = \int_0^{a/2}\phi_1^*(x)\psi(x)\,dx = \frac{2}{a}\int_0^{a/2}\sin^2\frac{\pi x}{a}\,dx = \frac{1}{a}\int_0^{a/2}\left(1-\cos\frac{2\pi x}{a}\right)dx$$

$$= \frac{1}{a}\left[x - \frac{\sin\frac{2\pi x}{a}}{\frac{2\pi}{a}}\right]_0^{a/2} = \frac{1}{a}\left[\frac{a}{2}\right] = \frac{1}{2}$$

Probability, $P = |<\phi_1|\psi>|^2 = \left(\frac{1}{2}\right)^2 = \frac{1}{4}$

Problem: Consider a physical system whose state is spaned by orthonormal basis vectors $\upsilon_1, \upsilon_2, \upsilon_3$ An operator A in this space is defined by :

$$A\upsilon_1 = \upsilon_1 + 2\upsilon_2;\quad A\upsilon_2 = \upsilon_2 + 2\upsilon_3;\quad A\upsilon_3 = 2\upsilon_1 + 2\upsilon_2 - \upsilon_3$$

Find the eigenvalues and matrix representation of matrix A.

$$A_{mn} = <\upsilon_m|\hat{A}|\upsilon_m> \qquad A = \begin{bmatrix} 1 & 0 & 2 \\ 2 & 1 & 2 \\ 0 & 2 & -1 \end{bmatrix}$$

Problem: For a 1-D Harmonic oscillator

(i) Calculate the expectation value of x^4

(ii) Calculate the $< E_n >$ if $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 - \lambda\hat{x}^4$

Soln. (i) $< x^4 > = < n|\hat{x}^4|n >$

$$=\langle n|\hat{x}^2\hat{I}\hat{x}^2|n\rangle=\sum_{m=0}^{\infty}\langle n|\hat{x}^2|m\rangle\langle m|\hat{x}^2|n\rangle$$

$$=\sum_{m=0}^{\infty}|\langle m|\hat{x}^2|n\rangle|^2=\left(\frac{\hbar}{2m\omega}\right)^2\sum_{m=0}^{\infty}|\langle m|\left(\hat{a}^2+\hat{a}^{\dagger 2}+2\hat{a}^{\dagger}\hat{a}+1\right)|n\rangle|^2$$

$$=\left(\frac{\hbar}{2m\omega}\right)^2\sum_{m=0}^{\infty}|\langle m|\hat{a}^2|n\rangle+\langle m|\hat{a}^{\dagger 2}|n\rangle+\langle m|2\hat{a}\hat{a}^{\dagger}|n\rangle+\langle m|n\rangle|^2$$

$$=\frac{\hbar^2}{4m^2\omega^2}\left[n(n-1)+(2n+1)^2+(n+1)(n+2)\right]=\frac{\hbar^2}{4m^2\omega^2}\left(6n^2+6n+3\right)$$

(ii) $\langle E_n\rangle=\langle n|\hat{H}|n\rangle=\left(n+\frac{1}{2}\right)\hbar\omega-\frac{\lambda\hbar^2}{4m^2\omega^2}\left(6x^2+6n+3\right)$

Problem: A particle of mass m moves in the potential $V(x,y,z)=V_1(x,y)+V_2(z)$ where

$$V_1(x,y)=\frac{1}{2}m\omega^2\left(x^2+y^2\right) \qquad V_2(z)=\begin{cases}0 & 0\le z\le a\\ \infty & \text{elswhere}\end{cases}$$

(a) Calculate the energy levels and eigenfunctions)

(b) Let us now turn off $V_2(z)$. Calculate the degeneracy of n^{th} level.

Ans. (a) $E_n=\left(n_x+n_y+1\right)\hbar\omega$ (b) $g_n=(n+1)$

HYDROGEN ATOM

Hydrogen is a one electron system. An electron of mass m orbiting around the nucleus.

Here, $V(r)=-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$

For H_2 like atom: $V(r)=-\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$

Energy will be $E_n=-\frac{mz^2e^4}{2\left(4\pi\epsilon_0\right)^2\hbar^2n^2}=-\frac{13.6}{n^2}z^2\ eV$ (in M.K.S)

$$E_n=-\frac{mz^2e^4}{2\hbar^2n^2}\ (\text{in C.G.S.}) \qquad \text{As } \frac{1}{4\pi\epsilon_0}=1$$

Eigen function will be $\psi(\Omega,\theta,\phi)=R_{n\ell}(r)\,\theta_{\ell m}(\theta)\,\Phi_m(\phi)$

$$R_{n\ell}(r)=\sqrt{\left(\frac{2z}{na_0}\right)^3\frac{(n-\ell-1)}{2n\{(n+\ell)!\}^3}}\,e^{-\frac{zr}{na_0}}\left(\frac{2zr}{na_0}\right)^{\ell}L_{n+1}^{2\ell+1}\left(\frac{2zr}{na_0}\right)$$

$$\theta_{\ell m}(\theta)=\sqrt{(2\ell+1)\frac{(\ell-|m|)!}{(\ell+|m|)!}}\ P_{\ell}^{|m|}(\cos\theta) \qquad \Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

Here R depends only on r and quantum number are n and ℓ.

$\theta_{\ell m}(\theta)$ depends on θ and quantum numbers are ℓ, m, $\phi_m(\phi)$ depends on ϕ and magnetic quantum number 'm'.

Normalisation condition for 3-D: $\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \psi^* \psi\, r^2 dr \sin\theta d\theta d\phi$

As R $\rightarrow$ function of r only and independent of θ and ϕ.

Similarly, for θ and ϕ

So we can integrate it separately.

So we can take normalisation condition separately.

Wave functions for H_2 atom for first two or three states:

n	ℓ	m	state	Eigen function
1	0	0	1s	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	2s	$\psi_{200} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/a_0}$
2	1	0	2p	$\psi_{210} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0} r\cos\theta$
2	1	1	2p	$\psi_{211} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0} \sin\theta\, e^{i\phi}$

Exponential factor gives idea of n $\rightarrow e^{-\frac{r}{na_0}}$

$P_\ell^m(\cos\theta)$ gives idea of ℓ:

$e^{im_\ell\phi}$ gives idea of m_ℓ.

So, we can find quantum number from any wave function.

Problem : Calculate the expectation value of z-coordinate of position in the ground state of H_2 atom.

Soln. For ground state of H_2 atom.

$$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-\frac{r}{a_0}}$$

$$\langle z\rangle = \int \psi^* z \psi d\tau = \frac{1}{\pi a_0^3}\int e^{-\frac{2r}{a_0}} z d\tau = \frac{1}{\pi a_0^3}\int e^{-\frac{2r}{a_0}}(r\cos\theta) r^2 \sin\theta dr d\theta d\phi$$

$$= \frac{1}{\pi a_0^3}\int e^{-\frac{2r}{a_0}} r^3 \cos\theta \sin\theta d\theta d\phi dr = 0 \qquad \because \int_0^{\pi}\cos\theta\sin\theta d\theta = 0$$

Problem: Calculate the degeneracy for the n^{th} state of H_2 atom.

Soln. Wave function depend upon n, ℓ, m_ℓ

$$E_n = -\frac{13.6}{n^2} eV$$

For a given ℓ, m can take values $-\ell.....+\ell$

So, $(2\ell+1)$ value

For a given n: ℓ can take values:

$0,1,2.....n-1$

Therefore, we include all the possibilities, $g=\sum_{\ell=0}^{n-1}(2\ell+1)=n^2$

This is degeneracy when spin is not included

If spin is included, $g=\sum_{\ell=0}^{n-1}2(2\ell+1)=2n^2$

So, energy eigen state for H_2 atoms are degenerate and fold of degeneracy is n^2 or $2n^2$ depending on spin is not included or included.

Problem: Calculate the expectation value of position for the ground state of H_2 atom.

Soln. $\psi_{100}=\frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r}{a_0}}$

$$\langle r\rangle=\int\psi^* r\psi d\tau=\int\frac{1}{\pi a_0^3}e^{-\frac{2r}{a_0}}d\tau=\frac{1}{\pi a_0^3}\int e^{-\frac{2r}{a_0}}r^3dr.\sin\theta d\theta d\phi$$

$$=\frac{4\pi}{\pi a_0^3}\int_0^\infty e^{-\frac{2r}{a_0}}r^3dr=\frac{4\pi}{\pi a_0^3}\frac{3!}{\left(\frac{2}{a_0}\right)^4}=\frac{4}{a_0^3}\frac{6a_0^4}{16}=\frac{3}{2}a_0$$

Problem: Calculate the expectation value of $\frac{1}{r}$ for hydrogen atom in ground state.

Soln. $\left\langle\frac{1}{r}\right\rangle=\int\psi^*\frac{1}{r}\psi d\tau=\frac{1}{\pi a_0^3}\int e^{\frac{-2r}{a_0}}rdr\sin\theta d\theta d\phi=\frac{4\pi}{\pi a_0^3}\frac{1!}{\left(\frac{2}{a_0}\right)^2}=\frac{4}{a_0^3}\frac{a_0^2}{4}=\frac{1}{a_0}$

Note: Some results to calculate expectation values:

1. $\langle r\rangle=\langle n_\ell|r|n_\ell\rangle=\frac{1}{2}\left[3n^2-\ell(\ell+1)\right]a_0$
2. $\langle r^2\rangle=\langle n_\ell|r^2|n_\ell\rangle=\frac{1}{2}n^2\left[5n^2+1-3\ell(\ell+1)\right]a_0^2$
3. $\left\langle\frac{1}{r}\right\rangle=\frac{1}{n^2a_0}$
4. $\left\langle\frac{1}{r^2}\right\rangle=\frac{2}{n^3(2\ell+1)a_0^2}$

Problem: Three operators x, y and z satisfy the commutation relations.

$[x,y]=i\hbar z;\ [y,z]=i\hbar x;\ [z,x]=i\hbar y$

The set of all possible eigen values of the operator z in unit of $\hbar$ is:

(a) $\{0, \pm1, \pm2, \pm3, ...\}$ (b) $\left\{\frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, ...\right\}$

(c) $\left\{0, \pm\frac{1}{2}, \pm1, \pm\frac{3}{2}, \pm2, ...\right\}$ (d) $\left\{+\frac{1}{2}, \frac{+1}{2}\right\}$

Soln. If we consider x, y, z as L, S or J then all commutation results will be satisfied.
So, x, y and z may be either S L or J. All possible eigen values will be given by

(c) $0, \pm\frac{1}{2}, \pm1, \pm\frac{3}{2}, \pm2.....$

Problem: The ground state wave function of hydrogen atom is given by: $\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{\frac{r}{a_0}}$ (Where 'a_0' is constant)

If $P(r)\,dr$ is probability of finding the electron between r and r+dr.

(a) $P(r) \neq 0$ at $r = 0$ (b) $P(r) =$ maximum at $r = 0$

(c) $P(r)$ is maximum at $r = a$ (d) $\int_0^\infty P(r)\,dr = 1$

Soln. **Correct answer is (d)**

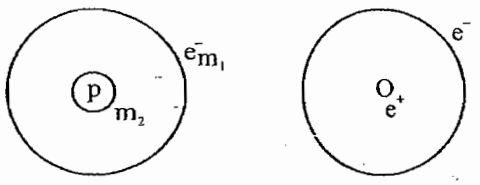
Then P(r) may not be maximum P(r) is maximum only when $a = a_0 = 0.53\text{Å}$

Problem: Given that binding energy of H_2 atom in the ground state is 13.6 eV. The binding energy for n = 2 state of the positronium atom.

$$E_n = -\frac{13.6}{n^2}; \quad E_1 = -13.6\text{ eV}; \quad E_2 = \frac{-13.6}{4} = -3.4\text{ eV}$$

This 3.4 eV is B.E. for n = 2 for H_2 atom.

In positronium atom: proton is replaced by e^+ (Positron).



H_2 atom

Reduced mass in H_2 atom $\mu = \frac{m_1 m_2}{m_1 + m_2}$

as $m_2 >> m_1$ $\therefore$ $\mu = \frac{m_1 m_2}{m_2} \simeq m_1$

Reduced mass in positronium atom.

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \therefore \quad \mu = \frac{m_1^2}{2m_1} = \frac{1}{2} m_1; \quad \mu = \frac{m}{2}$$

Since reduced mass is half.

As energy is directly proportional to mass

So, $\text{B.E.} = -\frac{3.4}{2} = -1.7\text{ eV}$

SPIN

Experimental need of spin:

- If we include the spin concept then there comes the concept of fine spectra.
- If we include nuclear spin then there comes the concept of hyperfine spectra.
- Anomalous Zeeman effect cannot be explain without concept of spin but normal Zeeman Effect can be explained.
- For ℓ, $m_\ell = +\ell \ldots\ldots\ldots\ldots -\ell$

Stern Gerlach Experiment: As atom is in ground state then a single beam is split by passing inhomogeneous $\bar{B}$.

$$m_\ell = +\ell \ldots\ldots\ldots\ldots -\ell$$

Interaction with $\bar{B}$ gives $2\ell+1$ lines.

- Neutral ground state $\ell = 0$

Unpaired electron also contributes.

Hence, shifting is not due to ℓ, m and other concept comes it is 'spin'.

$$m_j = +j \text{ to } -j = (2j+1) \text{ values}$$

Value of m_j are number of splitting lines. Total shifting is due to $\ell + s$.

$J = |\ell + s|$ to $|\ell - s|$. If $l = 0$, then also splitting is considered.

Stern-Gerlach Experiment:

If a neutral beam of Ag atoms is pass through inhomogeneous magnetic field then beam split into two parts due to the interaction of magnetic moment and magnetic field.

Beam split into $(2\ell+1)$ parts.

$$F = \nabla(\mu.B); \quad \mu_L = \frac{q}{2m}L; \quad \mu_L.B = \frac{q}{2m}L_z B$$

Where, $L_z = m_\ell \hbar$, $m_\ell = -\ell$ to $+\ell$

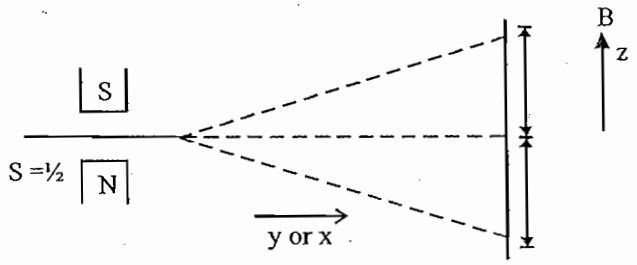
When silver atom in ground state then split into single beam.

If we consider electron (of spin $\frac{1}{2}$) then

$$j = |\ell + s| \text{ to } |\ell - s| = \frac{1}{2} \qquad \Rightarrow m_j = -\frac{1}{2}, +\frac{1}{2}$$

i.e. according to Stern Gerlach Experiment a single beam split into two parts i.e. Beam split in (2j+1) number of beams.

Deflection along the z-axis:

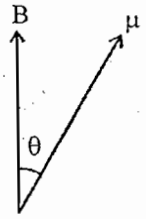


There are two component of spin for spin $\frac{1}{2}$ particle so there are two direction of beam splitting.

If $\vec{B}$ is along z-direction then no velocity along z-direction. It is along x or y direction then (force will be in the direction of $\vec{B}$ i.e. z-direction)

Deflection, $S = ut + \frac{1}{2}a_z t^2$

$\Rightarrow \quad S = \frac{1}{2}a_z t^2 \qquad \ldots(1) \qquad (u = 0 \text{ initially})$



Force, $F = \nabla(\mu.B)$

If μ is constant, then $F = \mu.\nabla B$; $F = \mu \nabla B \cos\theta$

Acceleration, $\boxed{a = \frac{F}{m} = \frac{\mu.\nabla B}{B} = \frac{\mu \cos\theta}{m}\frac{\partial B}{\partial z}}$

(1), $S = \frac{1}{2}a_z t^2$ (where a_z = acceleration along z-direction.)

If length of magnetic field region is L, particle velocity is 'v' then time $t = \frac{L}{v}$, then

$$S = \frac{1}{2}\frac{\mu \cos\theta}{m}\frac{\partial B}{\partial z}\left(\frac{L}{v}\right)^2 \qquad (\cos\theta = \pm 1)$$

This is the expression for the deflection in Stern-Gerlach experiment.

And separation between two beams is $\frac{1}{2}\frac{\mu}{m}\frac{\partial B}{\partial z}\frac{L^2}{v^2} - \left(-\frac{1}{2}\frac{\mu}{m}\frac{\partial B}{\partial z}\frac{L^2}{v^2}\right)$

$$\text{Separation} = \frac{\mu}{m}\frac{\partial B}{\partial z}\frac{L^2}{v^2}$$

Commutator bracket for spin operator:

- $\left[S_x, S_y\right] = i\hbar S_z$; $\left[S_y, S_z\right] = i\hbar S_x$; $\left[S_z, S_x\right] = i\hbar S_y$
- $S = \frac{1}{2}\hbar\sigma$ where σ = Pauli spin operator.
- Corresponding components

$$S_x = \frac{\hbar}{2}\sigma_x; \quad S_y = \frac{\hbar}{2}\sigma_y; \quad S_z = \frac{\hbar}{2}\sigma_z$$

- $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$

Eigen value of each component of spin is $\pm\frac{\hbar}{2}$. So, each σ^2 component will be 1.

- $[\sigma_x, \sigma_y] = 2i\sigma_z$; $[\sigma_y, \sigma_z] = 2i\sigma_x$; $[\sigma_z, \sigma_x] = 2i\sigma_y$

- Components of Pauli Spin operators anticommute i.e.

$\sigma_x\sigma_y + \sigma_y\sigma_x = 0$; $\sigma_y\sigma_z + \sigma_z\sigma_y = 0$; $\sigma_z\sigma_x + \sigma_x\sigma_z = 0$

$$\sigma_x\sigma_y + \sigma_y\sigma_x = \frac{1}{2i}\left[2i\sigma_x\sigma_y + 2i\sigma_y\sigma_x\right] = \frac{1}{2i}\left[\sigma_x\left(2i\sigma_y\right) + \left(2i\sigma_y\right)\sigma_x\right] = \frac{1}{2i}\left[\sigma_x(\sigma_z,\sigma_x) + (\sigma_z,\sigma_x)\sigma_x\right]$$

$$= \frac{1}{2i}\left[\sigma_x(\sigma_z\sigma_x - \sigma_x\sigma_z) + (\sigma_z\sigma_x - \sigma_x\sigma_z)\sigma_x\right]$$

$$= \frac{1}{2i}\left[\sigma_x\sigma_z\sigma_x - \sigma_x^2\sigma_z + \sigma_z\sigma_x^2 - \sigma_x\sigma_z\sigma_x\right] = \frac{1}{2i}\left[\sigma_x\sigma_z\sigma_x - \sigma_z + \sigma_z - \sigma_x\sigma_z\sigma_x\right]$$

$$\boxed{\sigma_x\sigma_y + \sigma_y\sigma_x = 0} \quad \Rightarrow \quad \boxed{\sigma_x\sigma_y = -\sigma_y\sigma_x}$$

- Also, $\sigma_x\sigma_y = i\sigma_z$; $\sigma_y\sigma_z = i\sigma_x$; $\sigma_z\sigma_x = i\sigma_y$

- Matrix form of Pauli Spin operators.

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

- If we change the reference axis then these matrix will be change. Here reference axis is z-axis.

- For spin $S = \frac{1}{2}$, $2S+1 = 2$

So there matrix are of 2×2 order.
If spin changes then these matrix forms will be change
e.g. if $S = 1$; $2S+1 = 3$, then 3×3 matrix.

- If matrix given then eigen function = ?

$$\hat{A}\psi = \lambda\psi$$

Any constant multiply with eigen function is the eigen value.

For $\sigma_z\psi = \lambda\psi$

Let, $\psi = \begin{bmatrix} a \\ b \end{bmatrix}$ where, components = number of spin component = 2

So, $\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = \lambda\begin{bmatrix} a \\ b \end{bmatrix}$

Eigen value of $\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ are ± 1

For $+1$, $\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} a \\ b \end{bmatrix}$ $\Rightarrow$ $1.a + 0.b = a$ & $0.a - b = b$

$\Rightarrow$ $b = -b$ not possible. Only for $b = 0$, it is possible.

$\Rightarrow$ $-2b = 0$; $b = 0$ always

So, for +1 eigenvalue of the eigen function is $\begin{bmatrix} a \\ 0 \end{bmatrix}$

Normalisation, $\langle \psi | \psi \rangle = 1$; $A^* \begin{bmatrix} a^* & 0 \end{bmatrix} A \begin{bmatrix} a \\ 0 \end{bmatrix} = 1$; $|A|^2 |a|^2 = 1$ and $A = \frac{1}{a}$

So, normalized eigen state is $|\psi(z)\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$

For -1 eigenvalue, z-component of eigenstate $= \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

i.e. $|\psi(z)\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}_{(+)}, \quad \begin{bmatrix} 0 \\ 1 \end{bmatrix}_{(-)}$

$|\psi(y)\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix}_{(+)}, \quad \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}_{(-)}$

$|\psi(x)\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}_{(+)}, \quad \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}_{(-)}$

$\downarrow$ $\downarrow$

for +ve eigen value for +ve eigen value.

- If this $|\psi(x)\rangle$ is the eigen state of S_x then eigen value will be $\frac{\hbar}{2}$.

The eigen state for spin component will be same as σ but eigen value will be different.

- Expectation value of any operator,

In Schrodinger notation, $\langle \hat{A} \rangle = \frac{\int \psi^* \hat{A} \psi d\tau}{\int \psi^* \psi d\tau}$

Dirac notation, $\langle \hat{A} \rangle = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi | \rangle}$

Problem: If a spin 1 particle is in the state $|m = 0\rangle$ w.r.t a quantisation axis $\hat{n}$. Which of the following is correct?

(a) $\langle \underline{S} \rangle = 0$ (b) $\langle \underline{S} \rangle = \hat{n}$ (c) $\langle \underline{S} \rangle = \sqrt{2}\hat{n}$ (d) $\langle \underline{S} \rangle = -\hat{n}$

Soln. $\underline{S} = S_x \hat{i} + S_y \hat{j} + S_z \hat{k}$

Suppose quantisation axis is z-axis.

So, $\langle S_x \rangle = 0$; $\langle S_y \rangle = 0$

$\langle S_z \rangle = \langle m = 0 | S_z | m = 0 \rangle = m\hbar = 0$ $(\because m = 0)$

So, $\langle \underline{S} \rangle = \langle S_x \rangle \hat{i} + \langle S_y \rangle \hat{j} + (S_z) \hat{k}$

$$\langle \underline{S} \rangle = 0$$

For a particular value of m_s, rotating about a particular angle so, expectation value of S will be zero in remaining two direction.

If $|m=1\rangle$ then if quantisation axis is z-axis, $\langle S_x \rangle = 0$, $\langle S_y \rangle = 0$

$$\langle S_z \rangle = \langle m=1 | S_z | m=1 \rangle = m\hbar = \hbar \qquad (\because m=1)$$

If we consider all angles together then always $m = 0$

Problem: For a spin $\frac{1}{2}$ particle, the expectation value of $S_x S_y S_z$ where (S_x, S_y, S_z are spin operators) is:

(a) $\frac{i\hbar^3}{8}$ (b) $\frac{-i\hbar^3}{8}$ (c) $\frac{i\hbar^3}{16}$ (d) $\frac{-i\hbar^3}{16}$

Soln. $S_x S_y S_z = \frac{\hbar}{2}\sigma_x \ \frac{\hbar}{2}\sigma_y \ \frac{\hbar}{2}\sigma_z = \frac{\hbar^3}{8}\sigma_x\sigma_y\sigma_z = \frac{\hbar^3}{8}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$

$$= \frac{\hbar^3}{8}\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} = \frac{\hbar^3}{8}\begin{bmatrix}i & 0\\ 0 & i\end{bmatrix} = \frac{i\hbar^3}{8}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix};$$

Taking $|\psi\rangle = \begin{bmatrix}a\\ b\end{bmatrix}$

Then, $\langle S_x S_y S_z \rangle = \begin{bmatrix}a^* b^*\end{bmatrix}\frac{\hbar^3 i}{8}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix} = \frac{\hbar^3 i}{8}\begin{bmatrix}a^* b^*\end{bmatrix}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix} = \frac{i\hbar^3}{8}\begin{bmatrix}a^* b^*\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix}$

$$= \frac{i\hbar^3}{8}\left[a^* a + b^* b\right] = \frac{i\hbar^3}{8}$$

Another method:

$$S_x S_y S_z = \frac{\hbar^3}{8}\sigma_x\sigma_y\sigma_z = \frac{\hbar^3}{8} i\,\sigma_z^2 = \frac{\hbar^3 i}{8}; \quad (\sigma_x\sigma_y = i\sigma_z); \quad (\sigma_z^2 = 1)$$

$$\langle S_x S_y S_z \rangle = \langle \psi | S_x S_y S_z | \psi \rangle = \left\langle \psi \middle| i\frac{\hbar^3}{8} \middle| \psi \right\rangle = \frac{i\hbar^3}{8}\langle \psi | \psi \rangle$$

$\langle \psi | \psi \rangle = 1$, then $\langle S_x S_y S_z \rangle = \frac{i\hbar^3}{8}$

Problem: A spin ½ particle in the state $S_z = \frac{\hbar}{2}$. The expectation value of S_x, S_x^2, S_y & S_y^2 are given by

(a) $0, 0, \frac{\hbar^2}{4}, \frac{\hbar^2}{4}$ (b) $0, \frac{\hbar^2}{4}, \frac{\hbar^2}{4}, 0$ (c) $0, \frac{\hbar^2}{4}, 0, \frac{\hbar^2}{4}$ (d) $\frac{\hbar^2}{4}, \frac{\hbar^2}{4}, 0, 0$

Soln. $S_z = \frac{\hbar}{2}$ corresponding eigen state $= \begin{bmatrix} 1 \\ 0 \end{bmatrix}$

Then, $\langle S_x \rangle = 0;\ \langle S_y \rangle = 0$ but $\langle S_x^2 \rangle$ and $\langle S_y^2 \rangle \neq 0$

So correct option is (c).

By method: $\langle S_x \rangle = [1,0]\frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2}[1,0]\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2}[1,0]\begin{bmatrix} 0 \\ 1 \end{bmatrix} = 0$ and $\langle S_x^2 \rangle = \frac{\hbar^2}{4}$

Now, $\langle S_x^2 \rangle = [1,0]\frac{\hbar^2}{4}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}^2\begin{bmatrix} 1 \\ 0 \end{bmatrix} = [1,0]\frac{\hbar^2}{4}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar^2}{4}[1,0]\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar^2}{4}$

So, $0, \frac{\hbar^2}{4}, 0, \frac{\hbar^2}{4}$ option (c) is correct.

Problem: An electron is in the state with spin wave function.

$\phi_s = \begin{bmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{bmatrix}$ is in the S_z representation. What is the probability of finding the z-component of its spin along the $-\hat{z}$ direction.

Soln. Expand ϕ_s in z-component of eigen function of S.

$$\phi_s = \begin{bmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{bmatrix} = \underset{\downarrow}{C_1}\begin{bmatrix} 1 \\ 0 \end{bmatrix} + \underset{\downarrow}{C_2}\begin{bmatrix} 0 \\ 1 \end{bmatrix}$$
$$\text{(along } +z) \qquad \text{(along } -z)$$

$C_1.1 + C_2.0 = \frac{\sqrt{3}}{2} \Rightarrow \sqrt{\frac{3}{2}} = C_1$

$C_1.0 + C_2.1 = \frac{1}{2} \Rightarrow \frac{1}{2} = C_2$

i.e. $\begin{bmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{bmatrix} = \frac{\sqrt{3}}{2}\begin{bmatrix} 1 \\ 0 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 0 \\ 1 \end{bmatrix}$

Probability of finding the particle $= \left|\frac{\sqrt{3}}{2}\right|^2 + \left|\frac{1}{2}\right|^2$

Probability of finding the z-component of spin along (-z) direction $= \frac{1}{4}$

Problem: Suppose a spin ½ particle in the state $|\phi\rangle = \frac{1}{\sqrt{6}}\begin{bmatrix} 1+i \\ 2 \end{bmatrix}$

What are the probabilities of getting $+\frac{\hbar}{2}$ & $-\frac{\hbar}{2}$. If

(i) z-component of spin is measured.
(ii) x-component of spin is measured.
(iii) Calculate the expectation value of S_x i.e. $\langle S_x \rangle$.

Soln. **(i) z-component of S.**

$$|\phi\rangle = \frac{1}{\sqrt{6}}\begin{bmatrix}1+i\\2\end{bmatrix} = C_1\begin{bmatrix}1\\0\end{bmatrix} + C_2\begin{bmatrix}0\\1\end{bmatrix} \Rightarrow \frac{1}{\sqrt{6}}(1+i) = C_1 \text{ and } \frac{1}{\sqrt{6}}2 = C_2$$

So, $$\frac{1}{\sqrt{6}}\begin{bmatrix}1+i\\2\end{bmatrix} = \frac{1}{\sqrt{6}}(1+i)\begin{bmatrix}1\\0\end{bmatrix} + \frac{1}{\sqrt{6}}2\begin{bmatrix}0\\1\end{bmatrix}$$

Probability of getting $+\frac{\hbar}{2} = |C_1|^2 = \left|\frac{1}{\sqrt{6}}(1+i)\right|^2 = \frac{1}{6}(1+i)(1-i) = \frac{1}{6}(1+1) = \frac{1}{3}$

Probability of getting $-\frac{\hbar}{2} = |C_2|^2 = \left|\frac{2}{\sqrt{6}}\right|^2 = \frac{4}{6} = \frac{2}{3}$

(ii) x-component of S.

$$\langle\phi| = \frac{1}{\sqrt{6}}\begin{bmatrix}1+i\\2\end{bmatrix} = C_1\frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix} + C_2\frac{1}{\sqrt{2}}\begin{bmatrix}1\\-1\end{bmatrix}$$

$$\Rightarrow \quad \frac{\frac{C}{\sqrt{2}} + \frac{C_2}{\sqrt{2}} = \frac{1}{\sqrt{6}}(1+i)}{\frac{C_1}{\sqrt{2}} - \frac{C_2}{\sqrt{2}} = \frac{1}{\sqrt{6}}(2)} \qquad \Rightarrow \sqrt{2}C_1 = \frac{1}{\sqrt{6}}(i+3) \qquad \Rightarrow C_1 = \frac{1}{\sqrt{2}}\left[\frac{(i+3)}{\sqrt{6}}\right]$$

$$2\frac{C_1}{\sqrt{2}} = \frac{1}{\sqrt{6}}[1+i+2]$$

On other hand, $2\frac{C_2}{\sqrt{2}} = \frac{1}{\sqrt{6}}(1+i-2) \Rightarrow \sqrt{2}C_2 = \frac{1}{\sqrt{6}}(i-1) \qquad \Rightarrow C_2 = \frac{1}{\sqrt{2}}\left[\frac{-1+i}{6}\right]$

Probability of getting $+\frac{\hbar}{2} = |C_1|^2 = \left|\frac{1}{\sqrt{2}}\left(\frac{i+3}{\sqrt{6}}\right)\right|^2 = \frac{1}{2}\frac{(3+i)(3-i)}{6} = \frac{1}{2}\frac{(9+1)}{6} = \frac{5}{6}$

Probability of getting $-\frac{\hbar}{2} = |C_2|^2 = \left|\frac{1}{\sqrt{2}}\frac{(-1+i)}{\sqrt{6}}\right|^2 = \frac{1}{6}$

(iii) $\langle S_x \rangle$ = probability × eigenvalue + probability × eigenvalue.

$$= P_1 \times \frac{\hbar}{2} + P_2 \times \left(\frac{-\hbar}{2}\right) = \frac{5}{6}\times\frac{\hbar}{2} - \frac{1}{6}\times\frac{\hbar}{2} = \frac{\hbar}{2\times 6}[5-1] = \frac{4\hbar}{2\times 6} = \frac{\hbar}{3}$$

Or, if probability is not given then

$$\langle S_x \rangle = \frac{1}{\sqrt{6}}(1-i,\ 2)\frac{\hbar}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\frac{1}{\sqrt{6}}\begin{bmatrix}1+i\\2\end{bmatrix} = \frac{\hbar}{12}[1-i,\ 2]\begin{bmatrix}2\\1+i\end{bmatrix} = \frac{\hbar}{12}[2(1-i)+2(1+i)] = \frac{\hbar}{3}$$

Problem: The wave function of an electron at a given time is given by $\psi = f(r,\theta)\, e^{2i\phi}\chi_{1/2}$. Calculate the average value of z-component of its magnetic moments.

Soln.

$\psi = f(r,\theta)\, e^{2i\phi}\, \chi_{1/2}$ $\left[f(r,\theta)\right.$ depends on r, θ; $e^{2i\phi}$ depends on φ and $\chi_{1/2}$ is the spin wave function$\left.\right]$

For H_2 atom, $\psi_{n\ell m} \propto e^{im_\ell \phi}$

$$\chi_{1/2} = \begin{bmatrix}1\\0\end{bmatrix} = |1/2, -1/2\rangle$$

$$\chi_{-1/2} = \begin{bmatrix}0\\1\end{bmatrix} = |1/2, -1/2\rangle$$

$$\left.\begin{aligned} L_z|\psi\rangle &= m_\ell \hbar\, |\psi \\ S_z|\psi\rangle &= m_s \hbar\, |\psi \end{aligned}\right\}$$

Expectation value of magnetic moment,

$$\mu = \underset{\text{depends on } L_z}{\underset{\Downarrow}{\mu_L}} + \underset{\text{depends on } S_z}{\underset{\Downarrow}{\mu_S}} = \frac{-e}{2m}L + \left(\frac{-2e}{2m}\right)S$$

$$\langle \mu_Z \rangle = \mu_{L_z} + \mu_{S_z} = \frac{-e}{2m}L_z + \left(\frac{-2e}{2m}\right)S_z = \frac{-e}{2m}\hbar m_\ell + \frac{-2e}{2m}\hbar m_s \quad \{\text{Bohr magneton } \mu_B = \frac{e\hbar}{2m}\}$$

$$\langle \mu_z \rangle = \langle \psi | \mu_z | \psi \rangle = \langle \psi | -\mu_B m_\ell | \psi \rangle - \left\langle \psi \middle| 2\mu_B \frac{1}{2} \middle| \psi \right\rangle$$

$$= -\mu_B m_\ell \langle \psi | \psi \rangle - 2\mu_B \frac{1}{2}\langle \psi | \psi \rangle = -2\mu_B - \mu_B = -3\mu_B$$

$$\langle \mu_Z \rangle = \langle \psi | \mu_{L_z} | \psi \rangle + \langle \psi | \mu_{S_z} | \psi \rangle = \left\langle \psi \middle| \left(\frac{-e}{2m}\right) L_z \middle| \psi \right\rangle + \left\langle \psi \middle| \left(\frac{-2e}{2m}\right) S_z \middle| \psi \right\rangle$$

$\psi = f(r,\theta) e^{2i\phi} \chi_{1/2}$

L_z will operate ψ then L_z operates only on $e^{2i\phi}$

S_z will operate on ψ then s_z operates only on $\chi_{1/2}$.

$$m_\ell = 2,\ L_z = m_\ell \hbar = 2\hbar \text{ and } S_z = m_s \hbar = \frac{\hbar}{2}$$

$$\therefore \quad \langle \mu_z \rangle = \left\langle \psi \middle| \left(\frac{-e}{2m}\right) 2\hbar \middle| \psi \right\rangle + \left\langle \psi \middle| \left(\frac{-2e}{2m}\right)\frac{1}{2}\hbar \middle| \psi \right\rangle = -2\mu_B \langle \psi | \psi \rangle - \mu_B \langle \psi | \bar{\psi} \rangle =$$

$$\Rightarrow \quad \langle \mu_Z \rangle = -3\mu_B$$

Problem: The wave function of an electron at a given time is

$$|\psi\rangle = f(r)[-2\chi_{1/2} + 3\chi_{-1/2}] \text{ or } f(r)\left[-2|\uparrow\rangle + 3|\downarrow\rangle\right]$$

Calulate the expectation value of z-component of magnetic moment.

Soln.

$|\psi\rangle = f(r)[-2\chi_{1/2} + 3\chi_{1/2}]$ $\left[f(r)\right.$ depends on r only and independent of θ and φ i.e. of ℓ and $m_\ell\left.\right]$

A function will be independent on θ and φ only if $\ell = 0$ and $m_\ell = 0$

If $f(r,\theta,\phi)$, then $n, \ell, m_\ell \neq 0$.

$|\psi\rangle$ is not normalised.

So, $|\psi\rangle = \dfrac{f(r)[-2\chi_{1/2}+3\chi_{-1/2}]}{\sqrt{4+9}} = \dfrac{f(r)[-2\chi_{1/2}+3\chi_{-1/2}]}{\sqrt{13}}$

$$\langle\psi| = \frac{f(r)}{\sqrt{13}}[-2\chi_{1/2}+3\chi_{-1/2}] \Rightarrow \langle\mu_z\rangle = \left\langle \psi\left|\underset{0}{\mu_{L_z}}\right|\psi\right\rangle + \langle\psi|\mu_{S_z}|\rangle$$

$$\langle\mu_z\rangle = \langle\psi|\mu_{S_z}|\psi\rangle = \left\langle\psi\left|\left(\frac{-2e}{2m}\right)S_z\right|\psi\right\rangle = \left\langle\left(\frac{-2\chi_{1/2}+3\chi_{-1/2}}{\sqrt{13}}\right)\left|\left(\frac{-2e}{2m}\right)S_z\right|\left(\frac{-2\chi_{1/2}+3\chi_{-1/2}}{\sqrt{13}}\right)\right\rangle$$

$$= \frac{1}{13}\left[4\left\langle\chi_{1/2}\left|\frac{-2e}{2m}S_z\right|\chi_{+1/2}\right\rangle + 9\left\langle\chi_{-1/2}\left|\frac{-2e}{2m}S_z\right|\chi_{-1/2}\right\rangle\right]$$

$$= \frac{1}{13}\left[4\frac{-2e}{2m}\frac{\hbar}{2}\langle\chi_{1/2}|\chi_{1/2}\rangle + 9\left(\frac{-2e}{2m}\right)\left(\frac{-\hbar}{2}\right)\langle\chi_{-1/2}|\chi_{-1/2}\rangle\right] = \frac{1}{13}[-4\mu_B+9\mu_B] = \frac{1}{13}5\mu_B$$

Problem: For Pauli Spin operator, prove that

(i) $e^{i\theta\vec{\sigma}.\hat{n}} = \cos\theta + i\vec{\sigma}.\hat{n}\sin\theta$, where θ is any arbitrary angle.

(ii) $e^{i\alpha\sigma_x}\sigma_z e^{-i\alpha\sigma_x} = \sigma_z\cos 2\alpha + \sigma_y \sin 2\alpha$, where α is any arbitrary angle.

Soln. **(i)** $e^{i\theta\vec{\sigma}.\hat{n}} = 1 + i\theta\vec{\sigma}.\hat{n} + \dfrac{(i\theta\vec{\sigma}.\hat{n})^2}{2!} + \dfrac{(i\theta\vec{\sigma}.\hat{n})^2}{3!} + \dfrac{(i\theta\vec{\sigma}.\hat{n})^4}{4!} + \ldots\ldots\ldots\ldots$

$$= 1 + \frac{(i\alpha\vec{\sigma}.\hat{n})^2}{2!} + \frac{(i\alpha\vec{\sigma}.\hat{n})^4}{4!} + \ldots\ldots\ldots\ldots (i\theta\vec{\sigma}.\hat{n}) + \frac{(i\theta\vec{\sigma}.\hat{n})^3}{3!} + \ldots\ldots$$

$(\vec{\sigma}.\hat{n})^2 = 1; \quad (\vec{\sigma}.\hat{n})^4 = 1$

$$e^{i\theta\vec{\sigma}.\hat{n}} = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} \ldots\ldots\ldots\ldots + i\vec{\sigma}.\hat{n}\left[\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \ldots\ldots\ldots\ldots\right]; \quad e^{i\theta\vec{\sigma}.\hat{n}} = \cos\theta + i\vec{\sigma}.\hat{n}\sin\theta$$

(ii) $e^{i\alpha\sigma_x}\sigma_z e^{i\alpha\sigma_x}$

Using $e^{i\theta\vec{\sigma}.\hat{n}} = \cos\theta + i\vec{\sigma}.\hat{n}\sin\theta$

$$e^{i\alpha\sigma_x}\sigma_z e^{-i\alpha\sigma_x} = (\cos\alpha + i\sigma_x \sin\alpha)\sigma_z(\cos\alpha - i\sigma_x\sin\alpha)$$

$$= \cos\alpha\sigma_z\cos\alpha - i\cos\alpha\sigma_z\sigma_x\sin\alpha + i\sigma_x\sin\alpha\sigma_z\cos\alpha + \sigma_x\sin\alpha\sigma_z\sigma_x\sin\alpha$$

$$= \sigma_z\cos^2\alpha + \sigma_x\sigma_z\sigma_x\sin^2\alpha + i\cos\alpha\sin\alpha[\sigma_x\sigma_z - \sigma_z\sigma_x]$$

$$= \sigma_z\cos^2\alpha - \sigma_z\sigma_x\sigma_x\sin^2\alpha + i\cos\alpha\sin\alpha[\sigma_x, \sigma_z]$$

$$= \sigma_z\cos^2\alpha - \sigma_z\sigma_x^2\sin^2\alpha + i\cos\alpha\sin\alpha(-2i\sigma_y)$$

$$= \sigma_z(\cos^2\alpha - \sin^2\alpha) + 2\cos\alpha\sin\alpha\sigma_y \qquad \{[\sigma_z, \sigma_x] = 2i\sigma\}$$

$$= \sigma_z\cos 2\alpha + \sin 2\alpha\sigma_y = \sigma_z\cos 2\alpha + \sigma_y\sin 2\alpha$$

Problem: The Hamiltonian of an electron in a constant magnetic field $\vec{B}$ is given by $\vec{H} = \mu\vec{\sigma}.\vec{B}$. Where μ is +ve constant and $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ donates the Pauli matrices. Let $\omega = \frac{\mu B}{\hbar}$ and I be 2×2 matrix then the operator $e^{\frac{iHt}{\hbar}}$ simplifies to

(a) $I\cos\frac{\omega t}{2} + \frac{i\vec{\sigma}.\vec{B}}{B}\sin\frac{\omega t}{2}$ (b) $I\cos\omega t + \frac{i\vec{\sigma}.\vec{B}}{B}\sin\omega t$ (c) $I\sin\omega t + \frac{i\vec{\sigma}.\vec{B}}{B}\cos\omega t$

(d) $I\sin 2\omega t + \frac{i\vec{\sigma}.\vec{B}}{2}\cos 2\omega t$ (e) $I\cos 2\omega t + \frac{i\vec{\sigma}.\vec{B}}{B}\sin 2\omega t$

Soln. $H = \mu\vec{\sigma}.\vec{B} = \mu\vec{\sigma}.B\hat{n} = \mu B\vec{\sigma}.\hat{n} \Rightarrow e^{\frac{iHt}{\hbar}} = e^{\frac{i\mu\vec{\sigma}.\vec{B}t}{\hbar}} = e^{\frac{i\mu\vec{\sigma}B.\hat{n}}{\hbar}} = e^{i\left(\frac{\mu Bt}{\hbar}\right)\vec{\sigma}.\hat{n}}$

On comparing with $e^{i\theta\vec{\sigma}.\hat{n}}$, we get, $\theta = \frac{\mu Bt}{\hbar} \Rightarrow \omega t = \frac{\mu Bt}{\hbar} \Rightarrow \omega = \frac{\mu B}{\hbar}$

So, $e^{\frac{iHt}{\hbar}} = \cos\left(\frac{\mu Bt}{\hbar}\right) + i\vec{\sigma}.\hat{n}\sin\left(\frac{\mu Bt}{\hbar}\right) = \cos\omega t + i\vec{\sigma}.\hat{n}\sin\omega t \Rightarrow e^{\frac{iHt}{\hbar}} = \cos\omega t + \frac{i\vec{\sigma}.\vec{B}}{B}\sin\omega t$

UNIT-V

ANGULAR MOMENTUM ALZEBRA

Orbital Angular Momentum:

In classical physics the angular momentum of a particle with momentum $\vec{p}$ and position $\vec{r}$ is defined by

$$\vec{L} = \vec{r} \times \vec{p} = (yp_z - zp_y)\hat{i} + (zp_x - xp_z)\hat{j} + (xp_y - yp_x)\hat{k} \qquad \ldots (1)$$

The orbital angular momentum operator $\hat{\vec{L}}$ can be obtained at once by replacing $\vec{r}$ and $\vec{p}$ by the corresponding operators in the position representation, $\hat{\vec{R}}$ and $\hat{\vec{P}} = -i\hbar\vec{\nabla}$

$$\hat{\vec{L}} = \hat{\vec{R}} \times \hat{\vec{P}} = -i\hbar \hat{\vec{R}} \times \vec{\nabla} \qquad \ldots (2)$$

The Cartesian components of $\hat{\vec{L}}$ are

$$\hat{L}_x = \hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y = -i\hbar\left(\hat{Y}\frac{\partial}{dz} - \hat{Z}\frac{\partial}{\partial y}\right) \qquad \ldots (3)$$

$$\hat{L}_y = \hat{Z}\hat{P}_x - \hat{X}\hat{P}_z = -i\hbar\left(\hat{Z}\frac{\partial}{dx} - \hat{X}\frac{\partial}{\partial z}\right) \qquad \ldots (4)$$

$$\hat{L}_z = \hat{X}\hat{P}_y - \hat{Y}\hat{P}_x = -i\hbar\left(\hat{X}\frac{\partial}{dy} - \hat{Y}\frac{\partial}{\partial x}\right) \qquad \ldots (5)$$

Clearly, angular momentum does not exist in a one-dimentinoal space. We should mention that the components, $\hat{L}_x, \hat{L}_y, \hat{L}_z$ and the square of $\hat{\vec{L}}$

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \qquad \ldots (6)$$

are all Hermitian.

Commutation relations:

Since, $\hat{X}$, $\hat{Y}$ and $\hat{Z}$ mutually commute and so do $\hat{P}_x, \hat{P}_y$ and $\hat{P}_z$

and since $\left[\hat{X}, \hat{P}_x\right] = i\hbar, \left[\hat{Y}, \hat{P}_y\right] = i\hbar, \left[\hat{Z}, \hat{P}_z\right] = i\hbar$ we have,

$$\left[\hat{L}_x, \hat{L}_y\right] = \left[\hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y, \hat{Z}\hat{P}_x - \hat{X}\hat{P}_z\right]$$

$$= \left[\hat{Y}\hat{P}_z, \hat{Z}\hat{P}_x\right] - \left[\hat{Y}\hat{P}_z, \hat{X}\hat{P}_z\right] - \left[\hat{Z}\hat{P}_y, \hat{Z}\hat{P}_x\right] + \left[\hat{Z}\hat{P}_y, \hat{X}\hat{P}_z\right]$$

$$= \hat{Y}\left[\hat{P}_z, \hat{Z}\right]\hat{P}_x + \hat{X}\left[\hat{Z}, \hat{P}_z\right]\hat{P}_y = i\hbar\left(\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x\right)$$

$$= i\hbar\hat{L}_z \qquad \ldots (7)$$

A similar calculation yields the other two commutation relations; but it is much simpler to infer them from equation (7) by means of a cyclic permutation of the xyz components, $x \to y \to z \to x$:

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y \qquad \ldots (8)$$

Since, $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$ do not commute, we cannot measure them simultaneously to arbitrary accuracy.

Note that commutation relations equation (8) were divided by expressing the orbital angular momentum in the position representation, but since these are operator relations, they must be valid in any representation. In the following section we are going to consider the general formalism of angular mo-

mentum, a formalism that is restricted to no particular representation.

Problem:

(a) Calculate the commutators $\left[\hat{X}, \hat{L}_x\right], \left[\hat{X}, \hat{L}_y\right]$, and $\left[\hat{X}, \hat{L}_z\right]$

(b) Calculate the commutators: $\left[\hat{P}_x, \hat{L}_x\right], \left[\hat{P}_x, \hat{L}_y\right]$ and $\left[\hat{P}_x, \hat{L}_z\right]$

(c) Use the results of (a) and (b) to calculate $\left[\hat{X}, \hat{\vec{L}}^2\right]$ and $\left[\hat{P}_x, \hat{\vec{L}}^2\right]$

Soln. (a) The only nonzero commutator which involves $\hat{X}$ and the various components of $\hat{L}_x, \hat{L}_y, \hat{L}_z$ is $\left[\hat{X}, \hat{P}_x\right] = i\hbar$

Having stated this result, we can easily evaluate the needed commutators. First, since $\hat{L}_x = \hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y$ involves no $\hat{P}_x$, the operator $\hat{X}$ commutes separately with $\hat{Y}, \hat{P}_z, \hat{Z}$ and $\hat{P}_y$; hence

$$\left[\hat{X}, \hat{L}_x\right] = \left[\hat{X}, \hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y\right] = 0 \qquad \ldots (9)$$

The evaluation of the other two commutators is straightforward.

$$\left[\hat{X}, \hat{L}_y\right] = \left[\hat{X}, \hat{Z}\hat{P}_x - \hat{X}\hat{P}_z\right] = \left[\hat{X}, \hat{Z}\hat{P}_x\right] = \hat{Z}\left[\hat{X}, \hat{P}_x\right] = i\hbar\hat{Z} \qquad \ldots (10)$$

$$\left[\hat{X}, \hat{L}_z\right] = \left[\hat{X}, \hat{X}\hat{P}_y - \hat{Y}\hat{P}_x\right] = -\left[\hat{X}, \hat{Y}\hat{P}_x\right] = -\hat{Y}\left[\hat{X}, \hat{P}_x\right] = -i\hbar\hat{Y} \qquad \ldots (11)$$

(b) The only commutator between $\hat{P}_x$ and the components of $\hat{L}_x, \hat{L}_y, \hat{L}_z$ that survives is again, $\left[\hat{P}_x, \hat{X}\right] = -i\hbar$. We may thus infer

$$\left[\hat{P}_x, \hat{L}_x\right] = \left[\hat{P}_x, \hat{Y}P_z - \hat{Z}\hat{P}_y\right] = 0 \qquad \ldots (12)$$

$$\left[\hat{P}_x, \hat{L}_y\right] = \left[\hat{P}_x, \hat{Z}P_x - \hat{X}\hat{P}_z\right] = -\left[\hat{P}_x, \hat{X}\hat{P}_z\right] = -\left[\hat{P}_x, \hat{X}\right]\hat{P}_z = i\hbar\hat{P}_z \qquad \ldots (13)$$

$$\left[\hat{P}_x, \hat{L}_z\right] = \left[\hat{P}_x, \hat{X}P_y - \hat{Y}\hat{P}_x\right] = \left[\hat{P}_x, \hat{X}\hat{P}_y\right] = \left[\hat{P}_x, \hat{X}\right]\hat{P}_y = -i\hbar\hat{P}_y \qquad \ldots (14)$$

(c) Using the commutators derived in (a) and (b), we infer

$$\begin{aligned}\left[\hat{X}, \hat{\vec{L}}^2\right] &= \left[\hat{X}, \hat{L}_x^2\right] + \left[\hat{X}, \hat{L}_y^2\right] + \left[\hat{X}, \hat{L}_z^2\right] \\ &= 0 + \hat{L}_y\left[\hat{X}, \hat{L}_y\right] + \left[\hat{X}, \hat{L}_y\right]\hat{L}_y + \hat{L}_z\left[\hat{X}, \hat{L}_z\right] + \left[\hat{X}, \hat{L}_z\right]\hat{L}_z \qquad \ldots (15) \\ &= i\hbar\left(\hat{L}_y\hat{Z} + \hat{Z}\hat{L}_y + \hat{Z}\hat{L}_y - \hat{L}_z\hat{Y} - \hat{Y}\hat{L}_y\right)\end{aligned}$$

$$\begin{aligned}\left[\hat{P}_x, \hat{\vec{L}}^2\right] &= \left[\hat{P}_x, \hat{L}_x^2\right] + \left[\hat{P}_x, \hat{L}_y^2\right] + \left[\hat{P}_x, \hat{L}_z^2\right] \\ &= 0 + \hat{L}_y\left[\hat{P}_x, \hat{L}_y\right] + \left[\hat{P}_x, \hat{L}_y\right]\hat{L}_y + \hat{L}_z\left[\hat{P}_x, \hat{L}_z\right] + \left[\hat{P}_x, \hat{L}_z\right]\hat{L}_z \qquad \ldots (16) \\ &= i\hbar\left(\hat{L}_y\hat{P}_z + \hat{P}_z\hat{L}_y - \hat{L}_z\hat{P}_y - \hat{P}_y\hat{L}_z\right)\end{aligned}$$

General formalism of angular momentum:

Let us introduce a more general angular momentum operator $\hat{\vec{J}}$ that is defined by its three components $\hat{J}_x, \hat{J}_y$ and $\hat{J}_z$, which satisfy the following commutation relations:

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z, \left[\hat{J}_y, \hat{J}_z\right] = i\hbar\hat{J}_x, \left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y \quad \ldots (17)$$

Since, $\hat{J}_x, \hat{J}_y$ and $\hat{J}_z$ do not mutually commute, they cannot be simultaneously diagonalized; that is they do not possess common eigenstates. The square of the angular momentum,

$$\hat{\vec{J}} = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \quad \ldots (19)$$

is a scalar operator, hence it commutes with $\hat{J}_x, \hat{J}_y$ and $\hat{J}_z$:

$$\left[\hat{\vec{J}}^2, \hat{J}_k\right] = 0 \quad \ldots (20)$$

where k stands for x, y and z. For instance, in the case k = x we have

$$\begin{aligned}\left[\hat{\vec{J}}^2, \hat{J}_x\right] &= \left[\hat{J}_x^2, \hat{J}_x\right] + \hat{J}_y\left[\hat{J}_y, \hat{J}_x\right] + \left[\hat{J}_y, \hat{J}_x\right]\hat{J}_y + \hat{J}_z\left[\hat{J}_z, \hat{J}_x\right] + \left[\hat{J}_z, \hat{J}_x\right]\hat{J}_z \\ &= \hat{J}_y\left(-i\hbar\hat{J}_z\right) + \left(-i\hbar\hat{J}_z\right)\hat{J}_y + \hat{J}_z\left(i\hbar\hat{J}_y\right) + \left(i\hbar\hat{J}_y\right)\hat{J}_z = 0\end{aligned} \quad \ldots (21)$$

Because $\left[\hat{J}_x^2, \hat{J}_x\right] = 0, \left[\hat{J}_y, \hat{J}_x\right] = -i\hbar\hat{J}_z$ and $\left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y$. We should note that the operators, $\hat{J}_x, \hat{J}_y, \hat{J}_z$ and $\hat{\vec{J}}^2$ are all Hermitian, their eigenvalues are real.

Eigenstates and eigenvalues of the angular momentum operator.

Since $\hat{\vec{J}}^2$ commutes with $\hat{J}_x, \hat{J}_y$ and $\hat{J}_z$, each component of $\vec{J}$ can be separately diagonalized (hence it has simultaneous eigenfunctions) with $\hat{\vec{J}}^2$. But since the components $\hat{J}_x, \hat{J}_y$ and $\hat{J}_z$ do not mutually commute, we can choose only one of them to be simultaneously diagonalized with $\hat{\vec{J}}^2$. By convention we choose $\hat{J}_z$. There is nothing special about the z-direction; we can just as well take $\hat{\vec{J}}^2$ and $\hat{J}_x$ or $\hat{\vec{J}}^2$ and $\hat{J}_y$.

Let us now look for the joint eigenstates of $\hat{\vec{J}}^2$ and $\hat{J}_z$ and their corresponding eigenvalues. Denoting the joint eigenstates by $|\alpha, \beta\rangle$ and the eigenvalues of $\hat{\vec{J}}^2$ and $\hat{J}_z$ by $\hbar^2\alpha$ and $\hbar\beta$, respectively, we have

$$\hat{\vec{J}}^2|\alpha, \beta\rangle = \hbar^2\alpha|\alpha, \beta\rangle, \quad \ldots (22)$$

and $$\hat{J}_z|\alpha, \beta\rangle = \hbar\beta|\alpha, \beta\rangle \quad \ldots (23)$$

The factor $\hbar$ is introduced so that α and β are dimensionless, recall that the angular momentum has the dimensions of $\hbar$ and that the physical dimensions of $\hbar$ are: $[\hbar] = \text{energy} \times \text{time}$. For simplicity, we will assume these eigenstates are orthonormal:

$$\langle\alpha', \beta'|\alpha, \beta\rangle = \delta_{\alpha',\alpha}\delta_{\beta',\beta} \quad \ldots (24)$$

Now, we need to introduce raising and lowering operators $\hat{J}_+$ and $\hat{J}_-$.

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \qquad \ldots (25)$$

This leads to

$$\hat{J}_x = \frac{1}{2}\left(\hat{J}_+ + \hat{J}_-\right), \qquad \hat{J}_y = \frac{1}{2i}\left(\hat{J}_+ - \hat{J}_-\right) \qquad \ldots (26)$$

hence, $\hat{J}_x^2 = \frac{1}{4}\left(\hat{J}_+^2 + \hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+ + \hat{J}_-^2\right)$, $\hat{J}_y^2 = -\frac{1}{4}\left(\hat{J}_+^2 - \hat{J}_+\hat{J}_- - \hat{J}_-\hat{J}_+ + \hat{J}_-^2\right)$ ... (27)

Using equation (17) we can easily obtain the following commutation relations.

$$\left[\hat{\vec{J}}^2, \hat{J}_\pm\right] = 0, \left[\hat{J}_+, \hat{J}_-\right] = 2\hbar\hat{J}_z, \quad \left[\hat{J}_z, \hat{J}_\pm\right] = \pm\hbar\hat{J}_\pm \qquad \ldots (28)$$

In addition, $\hat{J}_+$ and $\hat{J}_-$ satisfy

$$\hat{J}_+\hat{J}_- = \hat{J}_x^2 + \hat{J}_y^2 + \hbar\hat{J}_z = \hat{\vec{J}}^2 - \hat{J}_z^2 + \hbar\hat{J}_z \qquad \ldots (29)$$

$$\hat{J}_-\hat{J}_+ = \hat{J}_x^2 + \hat{J}_y^2 - \hbar\hat{J}_z = \hat{\vec{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z \qquad \ldots (30)$$

These relations lead to

$$\hat{\vec{J}}^2 = \hat{J}_\pm\hat{J}_\mp + \hat{J}_z^2 \mp \hbar_z \qquad \ldots (31)$$

which in turn yield

$$\hat{\vec{J}}^2 = \frac{1}{2}\left(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\right) + \hat{J}_z^2 \qquad \ldots (32)$$

Let us see how $\hat{J}_\pm$ operate on $|\alpha, \beta\rangle$. First, since $\hat{J}_\pm$ do not commute with $\hat{J}_z$, the kets $|\alpha, \beta\rangle$ are not eigenstates of $\hat{J}_\pm$. Using the relations equation (28), we have

$$\hat{J}_z\left(\hat{J}_\pm|\alpha, \beta\rangle\right) = \left(\hat{J}_\pm\hat{J}_z \pm \hbar\hat{J}_\pm\right)|\alpha, \beta\rangle = \hbar(\beta \pm 1)\left(\hat{J}_\pm|\alpha, \beta\rangle\right) \qquad \ldots . (33)$$

hence that ket $\left(\hat{J}_\pm|\alpha, \beta\rangle\right)$ is an eigenstates of $\hat{J}_z$ with eigenvalues $\hbar(\beta \pm 1)$. Now since $\hat{J}_z$ and $\hat{\vec{J}}^2$ commute, $\left(\hat{J}_\pm|\alpha, \beta\rangle\right)$ must also be an eigenstates of $\hat{\vec{J}}^2$. The eigenstates of $\hat{\vec{J}}^2$ when acting on $\hat{J}_\pm|\alpha, \beta\rangle$ can be determined by making use of the commutator $\left[\hat{\vec{J}}^2, \hat{J}_\pm\right] = 0$. The state $\left(\hat{J}_\pm|\alpha, \beta\rangle\right)$ is also an eigenstates of $\hat{\vec{J}}^2$ with eigenvalue $\hbar^2\alpha$:

$$\hat{\vec{J}}^2\left(\hat{J}_\pm|\alpha, \beta\rangle\right) = \hat{J}_\pm\hat{\vec{J}}^2|\alpha, \beta\rangle = \hbar^2\alpha\left(\hat{J}_\pm|\alpha, \beta\rangle\right) \qquad \ldots (34)$$

From equation (33) and (34) we infer that when $\hat{J}_\pm$ acts on $|\alpha, \beta\rangle$, it does not affect the first quantum number α, but it raises or lowers the second quantum number β by one unit. That is $J_\pm|\alpha, \beta\rangle$ is proportional to $|\alpha, \beta \pm 1\rangle$:

$$\hat{J}_\pm|\alpha, \beta\rangle = C_{\alpha\beta}^{\pm}|\alpha, \beta \pm 1\rangle \qquad \ldots (35)$$

We will determine the constant $C_{\alpha\beta}^{\pm}$ later on.

Note that, for a given eigenvalues α of $\hat{\vec{J}}^2$, there exists an upper limit for the quantum number

β. This is due to the fact that the operator $\hat{J}^2 - \hat{J}_z^2$ is positive, since the matrix elements of $\hat{J}^2 - \hat{J}_z^2 = \hat{J}_x^2 + \hat{J}_y^2$ are ≥ 0; we can therefore write,

$$\left\langle \alpha, \beta \left| \hat{J}^2 - \hat{J}_z^2 \right| \alpha, \beta \right\rangle = \hbar^2 \left(\alpha - \beta^2 \right) \geq 0, \Rightarrow \alpha \geq \beta^2 \qquad \ldots (36)$$

Since β has upper limit β_{max}, there must exist a state $|\alpha, \beta_{max}\rangle$ which cannot be raised further.

$$\hat{J}_+ |\alpha, \beta_{max}\rangle = 0 \qquad \ldots (37)$$

Using this relation along with $\hat{J}_- \hat{J}_+ = \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z$, we see that $\hat{J}_- \hat{J}_+ |\alpha, \beta_{max}\rangle = 0$ or

$$\left(\hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z \right) |\alpha, \beta_{max}\rangle = \hbar^2 \left(\alpha - \beta_{max}^2 - \beta_{max} \right) |\alpha, \beta_{max}\rangle; \qquad \ldots (38)$$

hence, $\alpha = \beta_{max} \left(\beta_{max} + 1 \right)$ $\ldots (39)$

After n successive applications of $\hat{J}_-$ on $|\alpha, \beta_{max}\rangle$, we must be able to reach a state $|\alpha, \beta_{min}\rangle$ which cannot be lowered further.

$$\hat{J}_- |\alpha, \beta_{min}\rangle = 0 \qquad \ldots .(40)$$

Using $\hat{J}_+ \hat{J}_- = \hat{J}^2 - \hat{J}_z^2 + \hbar \hat{J}_z$, and by analogy with equation (38) and (39), we infer that

$$\alpha = \beta_{min} \left(\beta_{min} - 1 \right) \qquad \ldots (41)$$

Comparing equation (39) and (41) we obtain

$$\beta_{max} = -\beta_{min} \qquad \ldots (42)$$

Since β_{min} was reached by n applications of $\hat{J}_-$ on $|\alpha, \beta_{max}\rangle$, if follows that

$$\beta_{max} = \beta_{min} + n \qquad \ldots (43)$$

and since $\beta_{min} = -\beta_{max}$ we conclude that

$$\beta_{max} = \frac{n}{2} \qquad \ldots (44)$$

Hence β_{max} can be integer or half-odd-integer, depending on n being even or odd.

It is now appropriate to introduce the notation j and m to denote β_{max} and β, respectively.

$$j = \beta_{max} = \frac{n}{2}, \; m = \beta \qquad \ldots (45)$$

hence the eigenvalue of $\hat{J}^2$ is given by

$$\alpha = j(j+1) \qquad \ldots (46)$$

Now since $\beta_{min} = -\beta_{max}$, and with n positive, we infer that the allowed values of m be between $-j$ and $+j$:

$$-j \leq m \leq j \qquad \ldots (47)$$

The results obtained thus far can be summarized as follows: the eigenvalues of $\hat{J}^2$ and J_z corresponding to the joint eigenvalues $|j, m\rangle$ are given, respectively by $\hbar^2 j(j+1)$ and $\hbar m$:

$$\hat{J}^2|j,m\rangle = \hbar^2 j(j+1)|j,m\rangle \text{ and } \hat{J}_z|j,m\rangle = \hbar m|j,m\rangle \quad \ldots (48)$$

where j = 0, 1/2, 3/2, ... and m = –j(j–1), ..., j–1, j. So far each j there are 2j+1 values of m. For example, if j = 1 then m takes the three values –1, 0, 1; and if j = 5/2 then m takes the six values –5/2, –3/2, –1/2, ½, 3/2, 5/2. The values of j are either integer or half-integer. We see that the spectra of the angular momentum operators $\hat{J}^2$ and $\hat{J}_z$ are discrete. Since the eigenstates corresponding to different angular momenta are orthogonal, and since the angular momemtum spectra are discrete, the orthonormality condition is

$$\langle j', m' | j, m\rangle = \delta_{j',j}\delta_{m',m} \quad \ldots (49)$$

Let us now determine the eigenvalues of $\hat{J}_\pm$ within the $\{|j,m\rangle\}$ basis; $|j,m\rangle$ is not an eigenstate of $\hat{J}_\pm$. We can rewrite equation (35) as

$$\hat{J}_\pm|j,m\rangle = C^\pm_{jm}|j, m\pm1\rangle \quad \ldots (50)$$

We are going to derive $C^\pm_{jm}$ and then infer C^-_{jm}. Since $|j,m\rangle$ is normalized, we can use equation (50) to obtain the following two expressions

$$\left(\hat{J}_+|j,m\rangle\right)^\dagger\left(\hat{J}_m|j,m\rangle\right) = |C^+_{jm}|^2\langle j,m+1|j,m+1\rangle = |C^+_{jm}|^2 \quad \ldots (51)$$

$$|C^+_{jm}|^2 = \langle j,m|\hat{J}_-\hat{J}_+|j,m\rangle \quad \ldots (52)$$

But since $\hat{J}_-\hat{J}_+$ is equal to $\left(\hat{\vec{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z\right)$, and assuming the arbitrary phase of C^+_{jm} to be zero, we conclude that

$$C^+_{jm} = \sqrt{\left\langle j,m\left|\hat{\vec{J}}^2 - \hbar\hat{J}_z\right|j,m\right\rangle} = \hbar\sqrt{j(j+1)-m(m+1)} \quad \ldots (53)$$

By analogy with C^+_{jm} we can easily infer the expression for C^-_{jm};

$$C^-_{jm} = \hbar\sqrt{j(j+1)-m(m-1)} \quad \ldots (54)$$

Thus, the eigenvalue equations for $\hat{J}_+$ and $\hat{J}_-$ are given by

$$\hat{J}_\pm|j,m\rangle = \hbar\sqrt{j(j+1)-m(m\pm1)}|j,m\pm1\rangle \quad \ldots (55)$$

Or $$\hat{J}_\pm|j,m\rangle = \hbar\sqrt{j(j\mp m)(j\pm m+1)}|j,m\pm1\rangle \quad \ldots (56)$$

which in turn lead to the two relations:

$$\hat{J}_x|j,m\rangle = \frac{1}{2}\left(\hat{J}_+ + \hat{J}_-\right)|j,m\rangle$$

$$= \frac{\hbar}{2}\left[\sqrt{(j-m)(j+m+1)}|j,m+1\rangle + \sqrt{(j+m)(j-m+1)}|j,m-1\rangle\right] \quad \ldots (57)$$

$$\hat{J}_y|j,m\rangle = \frac{1}{2i}\left(\hat{J}_+ - \hat{J}_-\right)|j,m\rangle$$

$$= \frac{\hbar}{2i}\left[\sqrt{(j-m)(j+m+1)}|j,m+1\rangle - \sqrt{(j+m)(j-m+1)}|j,m-1\rangle\right] \quad \ldots (58)$$

The expectation values of $\hat{J}_x$ and $\hat{J}_y$ are therefore zero:

$$\left\langle j, m\left|\hat{J}_x\right| j, m\right\rangle = \left\langle j, m\left|\hat{J}_y\right| j, m\right\rangle = 0 \qquad \ldots (59)$$

The expectation values $\left\langle j, m\left|\hat{J}_x^2\right| j, m\right\rangle$ and $\left\langle j, m\left|\hat{J}_y^2\right| j, m\right\rangle$ are equal and given by

$$\left\langle \hat{J}_x^2 \right\rangle = \left\langle \hat{J}_y^2 \right\rangle = \frac{1}{2}\left[\left\langle j, m\left|\hat{\vec{J}}^2\right| j, m\right\rangle - \left\langle j, m\left|\hat{J}_z^2\right| j, m\right\rangle\right] = \frac{\hbar^2}{2}\left[j(j+1) - m^2\right] \qquad \ldots (60)$$

Problem: Calculate $\left[\hat{J}_x^2, \hat{J}_y\right]$, $\left[\hat{J}_z^2, \hat{J}_y\right]$ and $\left[\hat{\vec{J}}^2, \hat{J}_y\right]$; then show $\left\langle j, m\left|\hat{J}_x^2\right| j, m\right\rangle = \left\langle j, m\left|\hat{J}_y^2\right| j, m\right\rangle$

Soln. Since $\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z$ and $\left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y$, we have

$$\left[\hat{J}_x^2, \hat{J}_y\right] = \hat{J}_x\left[\hat{J}_x, \hat{J}_y\right] + \left[\hat{J}_x, \hat{J}_y\right]\hat{J}_x = i\hbar\left(\hat{J}_x\hat{J}_z + \hat{J}_z\hat{J}_x\right) = i\hbar\left(2\hat{J}_x\hat{J}_z + i\hbar\hat{J}_y\right) \qquad \ldots (61)$$

Similarly, since, $\left[\hat{J}_z, \hat{J}_y\right] = -i\hbar\hat{J}_x$ and $\left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y$, we have

$$\left[\hat{J}_z^2, \hat{J}_y\right] = \hat{J}_z\left[\hat{J}_z, \hat{J}_y\right] + \left[\hat{J}_z, \hat{J}_y\right] = -i\hbar\left[\hat{J}_z\hat{J}_x + {}_x\,\hat{J}_z\right] = -i\hbar\left(2\hat{J}_x\hat{J}_z + i\hbar\hat{J}_y\right) \qquad \ldots (62)$$

The previous two expressions yield,

$$\begin{aligned}\left[\hat{\vec{J}}^2, \hat{J}_y\right] &= \left[\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2, \hat{J}_y\right] = \left[\hat{J}_x^2, \hat{J}_y\right] + \left[\hat{J}_z^2, \hat{J}_y\right] \\ &= i\hbar\left(2\hat{J}_x\hat{J}_z + i\hbar\hat{J}_y\right) - i\hbar\left(2\hat{J}_x\hat{J}_z + i\hbar\hat{J}_y\right) = 0\end{aligned} \qquad \ldots (63)$$

Since we have,

$$\hat{J}_x^2 = \frac{1}{4}\left(\hat{J}_+^2 + \hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+ + \hat{J}_-^2\right),\ \hat{J}_y^2 = -\frac{1}{4}\left(\hat{J}_+^2 - \hat{J}_+\hat{J}_- - \hat{J}_-\hat{J}_+ + \hat{J}_-^2\right) \qquad \ldots (64)$$

and since $\left\langle j, m\left|\hat{J}_+^2\right| j, m\right\rangle = \left\langle j, m\left|\hat{J}_-^2\right| j, m\right\rangle = 0$, we can write

$$\left\langle j, m\left|\hat{J}_x^2\right| j, m\right\rangle = \frac{1}{4}\left\langle j, m\left|\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\right| j, m\right\rangle = \left\langle j, m\left|\hat{J}_y^2\right| j, m\right\rangle \qquad \ldots (65)$$

Matrix representation of Angular momentum:

The formalism of the previous section is general and independent of any particular representation. There are many ways to represent the angular momentum operators and their eigenstates. In this section we are going to discuss the matrix representation of angular momentum where eigenkets and operators will be represented by column vectors and square matrices, respectively. This is achieved by expanding states and operators in a discrete basis. We will see later how to represent the orbital angular momentum in the position representation.

Since $\hat{\vec{J}}^2$ and $\hat{J}_z$ is the unit matrix. The operators $\hat{\vec{J}}^2$ and $\hat{J}_z$ are diagonal in the basis given by their joint eigenstates.

$$\left\langle j', m'\left|\hat{\vec{J}}^2\right| j, m\right\rangle = \hbar^2 j(j+1)\delta_{j',j}\delta_{m',m} \qquad \ldots (67)$$

$$\left\langle j', m'\left|\hat{J}_z\right| j, m\right\rangle = \hbar m\delta_{j',j}\delta_{m',m} \qquad \ldots (68)$$

Thus, the matrices representing $\hat{\vec{J}}^2$ and $\hat{J}_z$ in the $\{|j, m\rangle\}$ eigenbasis are diagonal, their diagonal elements being equal to $\hbar^2 j(j+1)$ and $\hbar m$ respectively.

Now since the operators $\hat{J}_{\pm}$ do not commute with $\hat{J}_z$, they are represented in the $\{|j,m\rangle\}$ basis by matrices that are not diagonal.

$$\langle j',m'|\hat{J}_{\pm}|j,m\rangle = \hbar\sqrt{j(j+1)-m(m\pm1)}\,\delta_{j',j}\delta_{m',m} \qquad \ldots (69)$$

We can infer the matrices of $\hat{J}_x$ and $\hat{J}_y$ from equation (57) and (58)

$$\langle j',m'|\hat{J}_x|j,m\rangle = \frac{\hbar}{2}\left[\sqrt{j(j+1)-m(m+1)}\,\delta_{m',m+1}+\sqrt{j(j+1)-(m-1)}\,\delta_{m',m-1}\right]\delta_{j',j} \qquad \ldots (70)$$

$$\langle j',m'|\hat{J}_y|j,m\rangle = \frac{\hbar}{2}\left[\sqrt{j(j+1)-m(m+1)}\,\delta_{m',m+1}-\sqrt{j(j+1)-(m-1)}\,\delta_{m',m-1}\right]\delta_{j',j} \qquad \ldots (71)$$

Example: Consider the case where $j = 1$

(a) Find the matrices representing the operators $\hat{\vec{J}}^2$, $\hat{J}_z$ and verify that they form an orthonormal and complete basis.

(c) Use the matrices of $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ to calculate $\left[\hat{J}_x,\hat{J}_y\right]$, $\left[\hat{J}_y,\hat{J}_z\right]$ and $\left[\hat{J}_z,\hat{J}_x\right]$

(d) Verify that $\hat{J}_z^3 = \hbar^2\hat{J}_z$ and $\hat{J}_{\pm}^3 = 0$

Soln. (a) For $j = 1$ then allowed values of m are -1, 0, 1. The joint eigenstates of $\hat{\vec{J}}^2$ and $\hat{J}_z$ are $|1,-1\rangle$, $|1,0\rangle$ and $|1,1\rangle$. The matrix representations of the operators $\hat{\vec{J}}^2$ and $\hat{J}_z$ can be inferred from equation (67) and (68)

$$\hat{\vec{J}}^2 = \begin{pmatrix} \langle 1,1|\hat{\vec{J}}^2|1,1\rangle & \langle 1,1|\hat{\vec{J}}^2|1,0\rangle & \langle 1,1|\hat{\vec{J}}^2|1,-1\rangle \\ \langle 1,0|\hat{\vec{J}}^2|1,1\rangle & \langle 1,0|\hat{\vec{J}}^2|1,0\rangle & \langle 1,0|\hat{\vec{J}}^2|1,-1\rangle \\ \langle 1,-1|\hat{\vec{J}}^2|1,1\rangle & \langle 1,-1|\hat{\vec{J}}^2|1,0\rangle & \langle 1,-1|\hat{\vec{J}}^2|1,-1\rangle \end{pmatrix} = 2\hbar^2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \ldots (72)$$

$$\hat{J}_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \ldots (73)$$

Similarly, using (59), we can ascertain that the matrices of $\hat{J}_+$ and $\hat{J}_-$ are given by

$$\hat{J}_- = \hbar\sqrt{2}\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix},\quad \hat{J}_+ = \hbar\sqrt{2}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \qquad \ldots (74)$$

The matrices for $\hat{J}_x$ and $\hat{J}_y$ in the $\{|j,m\rangle\}$ basis result immediately from the relations, $\hat{J}_x = \left(\hat{J}_+ + \hat{J}_-\right)/2$ and $\hat{J}_y = i\left(\hat{J}_- - \hat{J}_+\right)/2$.

$$\hat{J}_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{J}_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \qquad \ldots (75)$$

(b) The joint eigenvectors $\hat{J}^2$ and $\hat{J}_z$ can be obtained as follows. The matrix equation of $\hat{J}_z|j,m\rangle = m\hbar|j,m\rangle$ is

$$\hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} a \\ b \\ c \end{pmatrix} = m\hbar\begin{pmatrix} a \\ b \\ c \end{pmatrix} \Rightarrow \begin{matrix} \hbar a = m\hbar a \\ 0 = m\hbar b \\ -\hbar c = m\hbar c \end{matrix} \qquad \ldots (76)$$

The normalized solutions to these equation for $m = 1, 0, -1$ are respectively given by $a = 1, b = c = 0$; $a = 0, b = 1, c = 0$ and $a = b = 0, c = 1$; that is,

$$|1,1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |1,0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |1,-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad \ldots (77)$$

We can verify that they are complete

$$\sum_{m=-1}^{1} |1,m\rangle\langle 1,m| = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}(0\,0\,1) + \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}(0\,1\,0) + \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}(1\,0\,0) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \ldots (78)$$

(c) Using the matrices (75) we have,

$$\hat{J}_x\hat{J}_y = \frac{\hbar^2}{2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} = \frac{\hbar^2}{2}\begin{pmatrix} i & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & -i \end{pmatrix} \qquad \ldots (79)$$

$$\hat{J}_y\hat{J}_x = \frac{\hbar^2}{2}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \frac{\hbar^2}{2}\begin{pmatrix} -i & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & i \end{pmatrix}$$

Hence,

$$\hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x = \frac{\hbar^2}{2}\begin{pmatrix} 2i & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -2i \end{pmatrix} = i\hbar^2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} = i\hbar J_z$$

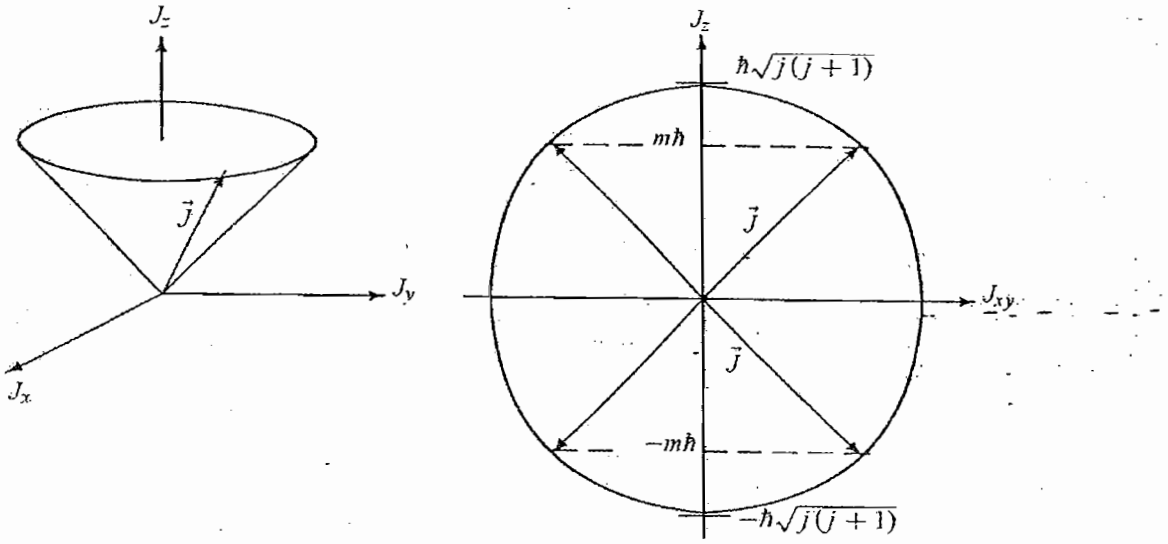
where the matrix of $\hat{J}_z$ is given by equation (73). A similar calculation leads to $\left[\hat{J}_y, \hat{J}_z\right] = i\hbar\hat{J}_x$ and $\left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y$

(d) The calculation of $\hat{J}_z^3$ and $\hat{J}_\pm^3$ is straightforward

$$\hat{J}_z^3 = \hbar^3\left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & -1 \end{pmatrix}\right]^3 = \hbar^3\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \hbar^3\hat{J}_z \qquad \ldots (83)$$

$$\hat{J}_+^3 = 2\hbar^3\sqrt{2}\left[\begin{pmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 0 & 0 & 0\end{pmatrix}\right]^3 = 2\hbar^3\sqrt{2}\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix} = 0 \qquad \ldots (84)$$

$$\hat{J}_-^3 = 2\hbar^3\sqrt{2}\left[\begin{pmatrix}0 & 0 & 0\\ 1 & 0 & 0\\ 0 & 1 & 0\end{pmatrix}\right]^3 = 2\hbar^3\sqrt{2}\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix} = 0 \qquad \ldots (85)$$



Eigenfunctions of Orbital Angular Momentum:

We now turn to the coordinate representation of the angular momentum. In this section, we are going to work within the spherical coordinate system. Let us denote the joint eigenstates of $\hat{\vec{L}}^2$ and $\hat{L}_z$ by $|\ell, m\rangle$

$$\hat{\vec{L}}^2|\ell, m\rangle = \hbar^2\ell(\ell+1)|, m\rangle \qquad \ldots (86)$$

$$\hat{L}_z|\ell, m\rangle = \hbar m|\ell, m\rangle \qquad \ldots (87)$$

The operators $\hat{L}_z, \hat{\vec{L}}^2, \hat{L}_\pm$, whose Cartesian comonents are listed in equation (3) to (5), can be expressed in terms of spherical coordinates as follows:

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi} \qquad \ldots (88)$$

$$\hat{\vec{L}}^2 \equiv -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \qquad \ldots (89)$$

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y = \pm\hbar e^{\pm i\varphi}\left[\frac{\partial}{\partial\theta} \pm i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\varphi}\right] \qquad \ldots (90)$$

Since the operators $\hat{L}_z$ and $\hat{\vec{L}}$ depend only on the angles θ and φ, their eigenstates depend only on θ and φ. Denoting their joint eigenstates by

$$\langle\theta\varphi|\ell, m\rangle = Y_{\ell m}(\theta, \varphi) \qquad \ldots (91)$$

where $Y_{\ell m}(\theta, \varphi)$ are continuous functions of θ and φ, we can rewrite the eigenvalue equtions (86) and (87) as follows.

$$\hat{L}^2 Y_{\ell m}(\theta, \varphi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta, \varphi) \quad \ldots (92)$$

$$\hat{L}_z Y_{\ell m}(\theta, \varphi) = m\hbar Y_{\ell m}(\theta, \varphi) \quad \ldots (93)$$

Since $\hat{L}_z$ depends only on φ as shown in (88), the previous two equations suggest that the eigenfunctions $Y_{\ell m}(\theta, \varphi)$ are separable:

$$Y_{\ell m}(\theta, \varphi) = \Theta_{\ell m}(\theta)\Phi_m(\varphi) \quad \ldots (94)$$

We ascertain that,

$$\hat{L}_{\pm} Y_{\ell m}(\theta, \varphi) = \hbar\sqrt{\ell(\ell+1) - m(m\pm1)}\, Y_{\ell m\pm1}(\theta, \varphi) \quad \ldots (95)$$

Eigenfunctions and eigenvalues of $\hat{L}_z$:

Inserting equation (94) into (93) we obtain $\hat{L}_z \Theta_{\ell m}(\theta)\Phi_m(\varphi) = m\hbar\Theta_{\ell m}(\theta)\Phi_m(\varphi)$. Now since $\hat{L}_z = -i\hbar\dfrac{\partial}{\partial\varphi}$, we have,

$$-i\hbar\Theta_{\ell m}(\theta)\frac{\partial\Phi_m(\varphi)}{\partial\varphi} = m\hbar\Theta_{\ell m}(\theta)\Phi_m(\varphi) \quad \ldots (96)$$

which reduces to

$$-i\frac{\partial\Phi_m(\varphi)}{\partial\varphi} = m\Phi_m(\varphi) \quad \ldots (97)$$

The normalized solutions of this equation are given by

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \quad \ldots (98)$$

where $\dfrac{1}{\sqrt{2\pi}}$ is the normalization constant,

$$\int_0^{2\pi} d\varphi \Phi_m^*(\varphi)\Phi_m(\varphi) = \delta_{m',m} \quad \ldots (99)$$

For $\Phi_m(\varphi)$ to be single-valued, it must be periodic in φ with period 2π, $\Phi_m(\varphi+2\pi) = \Phi_m(\varphi)$; hence,

$$e^{im(\varphi+2\pi)} = e^{im\varphi} \quad \ldots (100)$$

This relation shows that the expectation value of $\hat{L}_z$, $\ell_z = \langle \ell, m|\hat{L}_z|\ell, m\rangle$, is restricted to a discrete set of values.

$$\ell_z = m\hbar, \qquad m = 0, \pm1, \pm2, \pm3, \ldots\ldots \quad \ldots (101)$$

Thus, the value of m vary from $-\ell$ to ℓ:

$$m = -\ell, -(\ell-1), -(\ell-2), \ldots\ldots, 0, 1, 2, \ldots\ldots, \ell-2, \ell, -1, \ell \quad \ldots (102)$$

Hence the quantum number l must also be an integer. This is expected since the orbital angular momentum must have integer values.

Eigenfunctions of $\hat{L}^2$:

Let us now focus on determining the eigenfunctions $\Theta_{\ell m}(\theta)$ of $\hat{L}^2$. We are going to follow two methods. The first method involves differential equations and gives $\Theta_{\ell m}(\theta)$ in terms of the well-knonw associated Legendre functions. The second method is algebraic, it deals with the operators $\hat{L}_{\pm}$ and enables an explicit construction of $Y_{\ell m}(\theta, \varphi)$, the spherical harmonics.

First method for determining the eigenfunctions of $\hat{L}^2$:

We begin by applying $\hat{L}^2$ of equation (89) to the eigenfunctions

$$Y_{\ell m}(\theta, \varphi) = \frac{1}{\sqrt{2\pi}} \Theta_{\ell m}(\theta) e^{im\varphi} \qquad \ldots (103)$$

This gives,

$$\hat{L} Y_{\ell m}(\theta, \varphi) = \frac{-\hbar^2}{\sqrt{2\pi}} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] \Theta_{\ell m}(\theta) e^{im\varphi}$$

$$= \frac{\hbar^2 \ell(\ell+1)}{\sqrt{2\pi}} \Theta_{\ell m}(\theta) e^{im\varphi} \qquad \ldots (104)$$

which, after eliminating the φ – dependence, reduces to

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta_{\ell m}(\theta)}{d\theta} \right) + \left[\ell(\ell+1) - \frac{m^2}{\sin^2\theta} \right] \Theta_{\ell m}(\theta) = 0 \qquad \ldots (105)$$

This equation is known as the Legendre differential equation. Its solutions can be expresed in terms of the associated Legendre functions $P_\ell^m(\cos\theta)$

$$\Theta_{\ell m}(\theta) = C_{\ell m} P_\ell^m(\cos\theta) \qquad \ldots (106)$$

Which are defined by

$$P_\ell^m(x) = (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_\ell(x) \qquad \ldots (107)$$

This shows that,

$$P_\ell^{-m}(x) = P_\ell^m(x), \qquad \ldots (108)$$

where $P_\ell(x)$ is the lth Legendre polynomial which is defined by the Rodrigues formula

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2 - \ell)^\ell \qquad \ldots (109)$$

We can obtain at once the first few Legendre polynomials

$$P_0(x) = 1, \qquad P_1(x) = \frac{1}{2} \frac{d(x^2-1)}{dx} = x \qquad \ldots (110)$$

$$P_2(x) = \frac{1}{8} \frac{d^2(x^2-1)^2}{dx^2} = \frac{1}{2}(3x^2-1), \quad P_3(x) = \frac{1}{48} \frac{d^3(x^2-1)^3}{dx^3} = \frac{1}{2}(5x^3-3x) \qquad \ldots (111)$$

$$P_4(x)=\frac{1}{8}\left(35x^4-30x^2+3\right),\quad P_5(x)=\frac{1}{8}\left(63x^5-70x^3+15x\right) \qquad \ldots(112)$$

The Legendre polynomials satisfy the following closure or completeness relation.

$$\frac{1}{2}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(x')P_\ell(x)=\delta(x-x') \qquad \ldots(113)$$

From equation (109) we can infer at once.

$$P_\ell(-x)=(-1)^\ell P_\ell(x) \qquad \ldots(114)$$

A similar calculation lead to the first few associated Legendre functions.

$$P_1^1(x)=\sqrt{1-x^2} \qquad \ldots(115)$$

$$P_1^2(x)=3x\sqrt{1-x^2},\quad P_2^2(x)=3\left(1-x^2\right) \qquad \ldots(116)$$

$$P_3^1(x)=\frac{3}{2}\left(5x^2-1\right)\sqrt{1-x^2},\quad P_3^2(x)=15x\left(1-x^2\right),\quad P_3^3(x)=15\left(1-x^2\right)^{3/2} \qquad \ldots(117)$$

where $P_\ell^0(x)=P_\ell(x)$, with $\ell=0,1,2,3.....$ The first few expressions for the associated Legendre functions and the Legendre polynomials are listed in Table below. Note that

$$P_\ell^m(-x)=(-1)^{\ell+m}P_\ell^m(x) \qquad \ldots(118)$$

The constant $C_{\ell m}$ of equation (106) can be determined from the orthonormalization condition,

$$\langle \ell', m' | \ell, m\rangle = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta Y^*_{\ell' m'}(\theta,\varphi) Y_{\ell m}(\theta,\varphi)=\delta_{\ell',\ell}\delta_{m',m} \qquad \ldots(119)$$

Which can be written as

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta Y^*_{\ell' m'}(\theta,\varphi) Y_{\ell m}(\theta,\varphi)=\delta_{\ell',\ell}\delta_{m',m} \qquad \ldots(120)$$

Table-1: First few Legendre polynomials and associated Legendre functions.

Legendre polonomials	Associated Legendre functions
$P_0(\cos\theta)=1$	$P_1^1(\cos\theta)=\sin\theta$
$P_1(\cos\theta)=\cos\theta$	$P_2^1(\cos\theta)=3\cos\theta\sin\theta$
$P_2(\cos\theta)=\frac{1}{2}\left(3\cos^2\theta-1\right)$	$P_2^2(\cos\theta)=3\sin^2\theta$
$P_3(\cos\theta)=\frac{1}{2}\left(5\cos^3\theta-3\cos\theta\right)$	$P_3^1(\cos\theta)=\frac{3}{2}\sin\theta\left(5\cos^2\theta-1\right)$
$P_4(\cos\theta)=\frac{1}{8}\left(35\cos^4\theta-30\cos^2\theta+3\right)$	$P_3^2(\cos\theta)=15\sin^2\theta\cos\theta$
$P_5(\cos\theta)=\frac{1}{8}\left(63\cos^5\theta-70\cos^3\theta+15\cos\theta\right)$	$P_3^3(\cos\theta)=15\sin^3\theta$

This relation is known as the normalization condition of spherical harmonics. Using the form equation (103) for $Y_{\ell m}(\theta,\varphi)$

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \left|Y_{\ell m}(\theta,\varphi)\right|^2 = \frac{\left|C_{\ell m}\right|^2}{2\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \left|P_\ell^m(\cos\theta)\right|^2 = 1 \qquad \ldots (121)$$

From the theory of associated Legendre functions, we have

$$\int_0^{\pi} d\theta \sin\theta\, P_\ell^m(\cos\theta) P_{\ell'}^m(\cos\theta) = \frac{2}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}\delta_{\ell,\ell'} \qquad \ldots (122)$$

which is known as the normalization condition of associated Legendre functions. A combination of the previous two relations leads to an expression for the coefficient $C_{\ell m}$:

$$C_{\ell m} = (-1)^m \sqrt{\left(\frac{2\ell+1}{2}\right)\frac{(\ell-m)!}{(\ell+m)!}} \qquad (m \geq 0) \qquad \ldots (123.)$$

Inserting this equation into equation (106), we obtain the eigenfunctions of $\hat{L}^2$.

$$\Theta_{\ell m}(\theta) = (-1)^m \sqrt{\left(\frac{2\ell+1}{2}\right)\frac{(\ell-m)!}{(\ell+m)!}} P_\ell^m(\cos\theta) \qquad \ldots (124)$$

Finally, the joint eigenfunctions, $Y_{\ell m}(\theta,\varphi)$, of $\hat{L}$ and $\hat{J}_z$ can be obtained by substituting equation (98) and (124) into (94)

$$Y_{\ell m}(\theta,\varphi) = (-1)^m \sqrt{\left(\frac{2\ell+1}{4\pi}\right)\frac{(\ell-m)!}{(\ell+m)!}} P_\ell^m(\cos\theta) e^{im\varphi} \qquad (m \geq 0) \qquad \ldots (125)$$

These are called the normalized spherical harmonics.

Example:

(a) Use the relation $Y_{\ell 0}(\theta,\varphi) = \sqrt{(2\ell+1)/4\pi}\, P_\ell(\cos\theta)$ to find the expression of $Y_{30}(\theta,\varphi)$.

(b) Find the expression of Y_{30} in Cartesian coordinates.

(c) Use the expression of $Y_{30}(\theta,\varphi)$ to infer those of $Y_{3,\pm1}(\theta,\varphi)$

Soln. (a) From Table we have $P_3(\cos\theta) = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$; hence

$$Y_{30}(\theta,\varphi) = \sqrt{\frac{7}{4\pi}} P_3(\cos\theta) = \sqrt{\frac{7}{16\pi}}(5\cos^3\theta - 3\cos\theta) \qquad \ldots (126)$$

(b) Since $\cos\theta = \frac{z}{r}$, we have $5\cos^3\theta - 3\cos\theta = 5\cos\theta(5\cos^2\theta - 3) = z(5z^2 - 3r^2)/r^3$

hence,

$$Y_{30}(x,y,z) = \sqrt{\frac{7}{16\pi}}\frac{z}{r^3}(5z^2 - 3r^2) \qquad \ldots (127)$$

(c) To find Y_{31} from Y_{30}, we need to apply the ladder operator $\hat{L}_+$ on Y_{30} in two ways: first, algebrically

$$\hat{L}_{30} Y_{30} = \hbar\sqrt{3(3+1) - 0}\, Y_{31} = 2\hbar\sqrt{3}\, Y_{31} \qquad \ldots (128)$$

and hence, $$Y_{31} = \frac{1}{2\hbar\sqrt{3}}\hat{L}_+ Y_{30} \quad \ldots (129)$$

then we use the differential form (90) of $\hat{L}_+$:

$$\begin{aligned}\hat{L}_+ Y_{30}(\theta,\varphi) &= \hbar e^{i\varphi}\left[\frac{\partial}{\partial\theta} + i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\varphi}\right]Y_{30}(\theta,\varphi) \\ &= \hbar\sqrt{\frac{7}{16\pi}}e^{i\varphi}\left[\frac{\partial}{\partial\theta} + i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\varphi}\right]\left(5\cos^3\theta - 3\cos\theta\right) \\ &= -3\hbar\sqrt{\frac{7}{16\pi}}\sin\theta\left(5\cos^2\theta - 1\right)e^{i\varphi}\end{aligned} \quad \ldots (130)$$

Inserting equation (130) into (129) we end up with

$$Y_{31} = \frac{1}{2\pi\sqrt{3}}\hat{L}_+ Y_{30} = -\sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta - 1\right)e^{i\varphi} \quad \ldots (131)$$

Now, to find $Y_{3,-1}$ from Y_{30}, we also need to apply $\hat{L}_-$ on Y_{30} in two ways:

$$\hat{L}_- Y_{30} = \hbar\sqrt{3(3+1) - 0}\,Y_{3,-1} = 2\hbar\sqrt{3}\;Y_{3,-1} \quad \ldots (132)$$

and hence, $$Y_{3,-1} = \frac{1}{2\hbar\sqrt{3}}\hat{L}_- Y_{30} \quad \ldots (133)$$

then we use the differential form (90) of $\hat{L}_-$

$$\begin{aligned}\hat{L}_- Y_{30}(\theta,\varphi) &= -\hbar e^{-i\varphi}\left[\frac{\partial}{\partial\theta} - i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\varphi}\right]Y_{30}(\theta,\varphi) \\ &= -\hbar\sqrt{\frac{7}{16\pi}}\,e^{-i\varphi}\left[\frac{\partial}{\partial\theta} - i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\varphi}\right]\left(5\cos^3\theta - 3\cos\theta\right) \\ &= 3\hbar\sqrt{\frac{7}{16\pi}}\sin\theta\left(5\cos^2\theta - 1\right)e^{-i\varphi}\end{aligned} \quad \ldots (134)$$

Inserting (134) into (133), we obtain

$$Y_{3,-1} = \frac{1}{2\hbar\sqrt{3}}\hat{L}_- Y_{30} = \sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta - 1\right)e^{i\varphi} \quad \ldots (135)$$

Problem:

(a) Show that $\Delta J_x \Delta J_y = \hbar^2\left[j(j+1) - m^2\right]/2$, where $\Delta J_x = \sqrt{\left(\hat{J}_x^2\right) - \left(\hat{J}_x\right)^2}$ and the same for ΔJ_y

(b) Show that this relation is consistent with $\Delta J_x \Delta J_y \geq (\hbar/2)\left|\left\langle \hat{J}_z \right\rangle\right| = \hbar^2 m/2$

Soln. (a) First, note that $\left\langle \hat{J}_x \right\rangle$ and $\left\langle \hat{J}_y \right\rangle$ are zero, since

$$\left\langle \hat{J}_x \right\rangle = \frac{1}{2}\left\langle j,m\left|\hat{J}_+\right|j,m\right\rangle + \frac{1}{3}\left\langle j,m\left|\hat{J}_-\right|j,m\right\rangle = 0$$

As for $\langle \hat{J}_x^2 \rangle$ and $\langle \hat{J}_y^2 \rangle$, they are given by

$$\langle \hat{J}_x^2 \rangle = \frac{1}{4}\langle (\hat{J}_+ + \hat{J}_-) \rangle^2 = \frac{1}{4}(\hat{J}_+^2 + \hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+ + J_-^2)$$

$$\langle \hat{J}_y^2 \rangle = \frac{1}{4}\langle (\hat{J}_+ - \hat{J}_-) \rangle^2 = -\frac{1}{4}(\hat{J}_+^2 - \hat{J}_+\hat{J}_- - \hat{J}_-\hat{J}_+ + J_-^2)$$

Since, $\langle \hat{J}_+^2 \rangle = \langle \hat{J}_-^2 \rangle = 0$, we see that

$$\langle \hat{J}_x^2 \rangle = \frac{1}{4}\langle \hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+ \rangle = \langle \hat{J}_y^2 \rangle$$

Using the fact that,

$$\langle \hat{J}_x^2 \rangle + \langle \hat{J}_y^2 \rangle = \langle \hat{\vec{J}}^2 \rangle - \langle \hat{J}_z^2 \rangle$$

along with $\langle \hat{J}_x^2 \rangle + \langle \hat{J}_y^2 \rangle$, we see that

$$\langle \hat{J}_x^2 \rangle = \langle \hat{J}_y^2 \rangle = \frac{1}{2}\left[\langle \hat{\vec{J}}^2 \rangle - \langle \hat{J}_z^2 \rangle \right]$$

Now, since $|j,m\rangle$ is a joint eigensates of $\hat{\vec{J}}^2$ and $\hat{J}_z$ with eigenvalues $j(j+1)\hbar^2$ and $m\hbar$, we can easily see that the expressions of $\langle \hat{J}_x^2 \rangle$ and $\langle \hat{J}_y^2 \rangle$ are given by

$$\langle \hat{J}_x^2 \rangle = \langle \hat{J}_y^2 \rangle = \frac{1}{2}\left[\langle \hat{\vec{J}}^2 \rangle - \langle \hat{J}_z^2 \rangle \right] = \frac{\hbar^2}{2}\left[j(j+1) - m^2 \right]$$

Hence, $\Delta J_x \, \Delta J_y$ is given by

$$\Delta J_x \, \Delta J_y = \sqrt{\langle \hat{J}_x^2 \rangle \langle \hat{J}_y^2 \rangle} = \frac{\hbar^2}{2}\left[j(j+1) - m^2 \right]$$

(b) Since, $j \geq m$ (because $m = -j, j+1, \ldots, j-1, j$), we have

$$j(j+1) - m^2 \geq m(m+1) - m^2 = m$$

from which we infer that $\Delta J_x \Delta J_y \geq \hbar^2 \, m/2$, or $\Delta J_x \Delta J_y \geq \frac{\hbar}{2}|\hat{J}_z|$

UNIT-VI
IDENTICAL PARTICLES

We have already seen that two kinds of wave functions are possible: symmetric and anti symmetric. The complete wave function $\psi(1, 2, 3, ...N)$ of a system of noninteracting particles can be expressed as the product of the wave functions $\phi(1), \phi(2), \phi(3),...\phi(N)$ of the individual particles. That is.

$\psi(1, 2, 3, ...N) = \phi(1)\,\phi(2)\,\phi(3)...\phi(N)$

For simplicity, let us consider a two particle system. Suppose one of the particles is in the state a and the other one in the state 'b'.

If the particle 1 is in the state a and the particle 2 is in the state b, the wave function of the system is

$\psi_I = \phi_a(1)\,\phi_b(2)$

If the particle 2 is in the state a and the particle 1 is in the state b, the wave function is.

$\psi_{II} = \psi_a(2)\,\psi_b(1)$

Because the two particles are indistinguishable, we have no way to know at any moment whether ψ_I or ψ_{II} describes the system. Therefore a linear combination of ψ_I and ψ_{II} is the proper description of the system. Two such combination are possible, symmetric and antisymmetric.

$$\psi_S = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)\right]$$

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2)-\psi_a(2)\psi_b(1)\right]$$

In the symmetric case, both particles 1 and 2 can simultaneously exist in the same state a = b. In the anti symmetric case, if we set $a = b$, find that

$\psi_A = 0$

The two particles cannot be in the same quantum state (Pauli Principle)

Two particle system

$$\psi_S = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\varepsilon_1)\psi_{n2}(\varepsilon_2)+\psi_{n_1}(\varepsilon_2)\psi_{n_2}(\varepsilon_1)\right]$$

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)-\psi_{n_1}(\varepsilon_2)\psi_{n_2}(\varepsilon_2)\right]$$

where $n_1 \neq n_2$

Note that we can rewrite ψ_S as

$$\psi_S(\varepsilon_1, \varepsilon_2) = \frac{1}{\sqrt{2!}}\sum_P \hat{P}\psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)$$

where $\hat{p}$ is the permutation operator, and where the sum is over all possible permutations.

Similarly, we can rewrite ψ_A as

$$\psi_A(\varepsilon_1, \varepsilon_2) = \frac{1}{\sqrt{2!}}\sum_P (-1)^P \hat{P}\psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)$$

where $(-1)^P$ is + 1 for even permutation (i.e. when we interchange both ε_1 and ε_2 and also n_1 and n_2) and equal to –1 for an odd permutation (i.e. when we permute $\varepsilon_1, \varepsilon_2$ but not n1, n2 and vice versa). Note that

$$\psi_A(\varepsilon_1, \varepsilon_2) = \frac{1}{\sqrt{2!}}\begin{vmatrix}\psi_{n_1}(\varepsilon_1) & \psi_{n_2}(\varepsilon_2)\\ \psi_{n_2}(\varepsilon_1) & \psi_{n2}(\varepsilon_2)\end{vmatrix}$$

Three particle system:

$$\psi_S(\varepsilon_1, \varepsilon_2, \varepsilon_3) = \frac{1}{\sqrt{3!}}\sum_P \hat{P}\psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)\psi_{n_3}(\varepsilon_3)$$

$$\psi_A(\varepsilon_1, \varepsilon_2, \varepsilon_3) = \frac{1}{\sqrt{3!}}\sum_P (-1)^P \hat{P}\psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)\psi_{n_3}(\varepsilon_3)$$

$$= \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{n_1}(\varepsilon_1) & \psi_{n_2}(\varepsilon_2) & \psi_{n_3}(\varepsilon_3) \\ \psi_{n_2}(\varepsilon_1) & \psi_{n_2}(\varepsilon_2) & \psi_{n_2}(\varepsilon_3) \\ \psi_{n_3}(\varepsilon_1) & \psi_{n_3}(\varepsilon_2) & \psi_{n_3}(\varepsilon_3) \end{vmatrix}$$

Many particle system:

$$\psi_S = \frac{1}{\sqrt{N!}} \sum_P \hat{P}\psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)...\psi_{n_N}(\varepsilon_N)$$

$$\psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)...\psi_{n_N}(\varepsilon_N)$$

$n_1 = n_2 = \ldots = n_{n_N}$, then

$$\psi_S = \prod_{i=1}^{N} \psi_n(\varepsilon_i)$$

When there a multiplicity in the number $n_1, n_2, \ldots n_N$ (i.e. when some of the number n_i occur more than once, we need to be careful and we have to avoid double counting. For example, if n_1 occurs N_2 Times, and so on, then the symmetric wave function is given by

$$\psi_S(\varepsilon_1, \varepsilon_2, ...\varepsilon_N) = \sqrt{\frac{N_1!N_2!...N_n!}{N!}} \sum_P \hat{P}\psi_{n_1}(\varepsilon_1)\psi_{n_2}(\varepsilon_2)...\psi_{n_N}(\varepsilon_N)$$

Identical Particles:

We designate as identical particles those particles that have the same mass, charge, spin etc. and behave in the same manner under equal physical conditions. Therefore, in contrast with macroscopic objects, it is not possible to distinguish between particles like elections (protons, pions) on the basis of their characteristics or their trajectory.

If we regard a Q.M. system of identical particles, we will not be able to relate a state ψ_n to a particle no. n; we will only be able to determine the state of the totality of all particles.

In the case of a system of N particles with spin, the wave function of these 4N co-ordinates (3N-space and N spin co-ordinates :

$$\psi = \psi(\vec{r}_1, s_1, \vec{r}_2, s_1, ...\vec{r}_N, s_N, t)$$

Since the system consists of identical particles, the physical state remains the same if the particles j and i are exchanged. This operation is carried out by the operator $\hat{P}_{ij}$:

$$\hat{P}_{ij}\psi(\vec{r}_1, s_1, ...\vec{r}_i, s_i, ...\vec{r}_j, s_i, ...\vec{r}_N, s_N, t) = \lambda\psi(\vec{r}_1, s_1, ...\vec{r}_j, s_j, ...\vec{r}_j, s_i, ...\vec{r}_N, s_N, t)$$

where λ is an arbitrary constant vector. A second exchange of the two particles recreates the original state. Hence

$$\hat{P}_{ij}^2\psi = \lambda^2\psi = \psi \Rightarrow \lambda = \pm 1$$

Two system of particles may exist; system with wave functions that change sign upon the exchange of two particles, and systems whose wave function remain unchanged.

either

$\hat{P}_{ij}^2\psi_s = \psi_s$ (symmetric) -OR- $\hat{P}_{ij}^2\psi_a = -\psi_a$ (antisymmetric)

A transition between symmetric and anti symmetric states is impossible. This is because the interaction between particles is symmetric under their exchange, hence

$$V(r_1, r_2 ... r_i ... r_j, r_N) = V(r_1, r_2, ...r_j, ...r_i, ...r_N)$$

The particles described by an anti symmetric wave function are called Fermions and those particles described b a symmetric wave function are called bosons.

Fermions Dermions have half-integer spin.

Bosons have Integer spin.

- **Exchange degeneracy**

Conside a system of N indentical particles without any interaction. The Schrodinger eq^n for such a system is

$$\left(\hat{H}_1+\hat{H}_2+...\hat{H}_N\right)\psi\ (\vec{r}_1 s_1,\vec{r}_2 s_2,...\vec{r}_N s_N)=E\,\psi\ (\vec{r}_1 s_1,\vec{r}_2 s_2,...\vec{r}_N s_N)\rightarrow(1)$$

The single particle Hamiltonians $\hat{H}_i(\vec{r}_i s_i)$ can be distinguished from each other by the fact that they act on different particles. If we designate ith the eigen function of the particle k by $\Phi_i(r_k, s_k)$

$$\hat{H}_k(\vec{r}_k,s_k)\Phi_i(\vec{r}_k,s_k)\ =\ E_i\Phi_i(\vec{r}_k,s_k),\ k=1,2,...N\ ;\ i=1,2,...\rightarrow(2)$$

The schriodinger *eq^n* is then solved by the product of single-particle wave functions :

$$\psi(\vec{r}_1,s_2,...\vec{r}_N s_N)\ =\ \Phi_{ij}\ (\vec{r}_2,s_2)\ ...\ \Phi_{i_N}(r_N,s_N)\rightarrow(3)$$

If there are n_i particles in the state $\Phi_{i\,i}$, then we will get for the eigenvalue of the total energy

$$E=\sum_i n_i E_i \text{ and } \sum_i n_i = N\ \rightarrow(4)$$

Because of the indistinguishafility of the particles we are not able to say which particle is in which state.

This means that there are $\left(\frac{N!}{n_1!n_2!n_3!\cdots}\right)$ combinations of the single particle wave function in (3) that give the same energy eigenvalue E. This is called exchange degeneracy

$$\psi_{boson}=\frac{1}{\sqrt{N!n_1\,n_2!}}\ ...\ \sum_{P=1}^{N!}P\Phi_{i_1}(\vec{r}_1 s_1)\,\Phi_{i_2}(\vec{r}_2 s_2)\Phi_{i_3}(\vec{r}_3 s_3)....\Phi_{i_N}(\vec{r}_N s_N)$$

Slater Determinant:

The antisymmetric wave function is best expressed in the form of a determinant. Slater's determinant is an N×N determinant consisting of a single paricle wave function arranged in the following way:

$$\psi_{fermion}\ \frac{1}{\sqrt{N!}}\begin{vmatrix} Q_{i_1}(r_1 s_1) & Q_{i2}(r_1 s_1) & Q_{i_3}(r_1 s_1) & Q_{i_4}(r_1 s_1) \\ Q_{i_1}(r_2 s_2) & Q_{i_1}(r_2 s_2) & ... & Q_{i_N}(r_2 s_2) \\ ... & ... & ... & ... \\ Q_{i_1}(r_N s_N) & Q_{i_2}(r_N s_N) & Q_{i_1}(r_N s_N) & Q_{i_1}(r_N s_N) \end{vmatrix}$$

Note : • each column contains the same single-particle wave function.
• each row contains the same argrement in the single particle wave function
The function will vanish if two particles occupy the same state.

Problem 1: Consider a system of three noninteracting particles that are confined to move in a one-dimensional infinite potential well of length a: $V(x)=0$ for $0<x<a$ and $V(x)=\infty$ for other values of x. Determine the energy and wave function of the ground state and the first and second excited states when the three particle are (a) spinless and distinguishable with $m_1<m_2<m_3$; (b) identical bosons; (c) identical spin ½ particles; and

Soln. **(a)** the total energy and wave function of a system of three non-interacting particles, confined to move in a 1-D infinite potential well are given by

$$E_{n_1,n_2,n_3}=\frac{\hbar^2\pi^2}{2a^2}\left(\frac{n_1^2}{m_1}+\frac{n_2^2}{m_2}+\frac{n_3^2}{m_3}\right)$$

$$\psi_{n_1,n_2,n_3}(x_1,x_2,x_3)=\sqrt{\frac{8}{a^3}}\sin\left(\frac{n_1\pi}{a}x_1\right)\sin\left(\frac{n_2\pi}{a}x_2\right)\sin\left(\frac{n_3\pi}{a}x_3\right)$$

The ground stae of the system corresponds to the case where all three particles occupy their respective ground state orbitals, $n_1 = n_2 = n_3 = 1$; hence

$$E^{(0)} = E_{1,1,1} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1}+\frac{1}{m_2}+\frac{1}{m_3}\right)$$

$$\psi^{(0)}(x_1,x_2,x_3) = \psi_{1,1,1}(x_1,x_2,x_3) = \sqrt{\frac{8}{a^3}}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{\pi}{a}x_3\right)$$

Since particle 3 has the highest mass, the first excited state corresponds to the case where particle 3 is in $n_3 = 2$, while particles 1 and 2 remain in $n_1 = n_2 = 1$.

$$E^{(1)} = E_{1,1,2} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1}+\frac{1}{m_2}+\frac{4}{m_3}\right)$$

$$\psi^{(1)}(x_1,x_2,x_3) = \psi_{1,1,2}(x_1,x_2,x_3) = \sqrt{\frac{8}{a^3}}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_3\right)$$

Similarly, the second excited state corresponds to the case where particles 2 and 3 are in $n_2 = n_3 = 2$, while particle 1 remains in $n_1 = 1$.

$$E^{(2)} = E_{1,2,2} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1}+\frac{4}{m_2}+\frac{4}{m_3}\right)$$

$$\psi^{(2)}(x_1,x_2,x_3) = \psi_{1,2,2}(x_1,x_2,x_3) = \sqrt{\frac{8}{a^3}}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{2\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_3\right)$$

(b) If all three particles were identical bosons, the ground state will correspond to all particles in the lowest state $n_1 = n_2 = n_3 = 1$.

$$E^{(0)} = E_{1,1,1} = 3\varepsilon_1 = \frac{3\hbar^2\pi^2}{2ma^2}$$

$$\psi^{(0)} = \psi_1(x_1)\psi_1(x_2)\psi_1(x_3) = \sqrt{\frac{8}{a^3}}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{\pi}{a}x_3\right)$$

Since, $\psi_n(x_i) = \sqrt{2/a}\,\sin(n\pi x_i/a)$

In the first excited state we have two particles in ψ_1 (each with energy $\varepsilon_1 = \hbar^2\pi^2/\left(2ma^2\right)$) and one in ψ_2 (with energy $\varepsilon_2 = 4\hbar^2\pi^2/\left(2ma^2\right) = 4\varepsilon_1$)

$$E^{(1)} = 2\varepsilon_1 + \varepsilon_2 = 2\varepsilon_1 + 4\varepsilon_1 = 6\varepsilon_1 = \frac{3\pi^2\hbar^2}{ma^2}$$

The wave function is somewhat tricky again. Since the particles are identical, we can no longer say which paticle is in which state; all we can say is that two particles are in ψ_1 and one in ψ_2. Since the value $n = 1$ occurs twice (two particles are in ψ_1), then

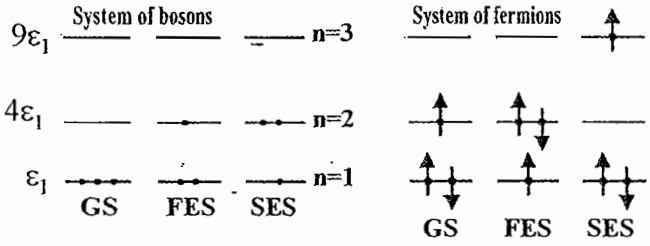
$$\psi^{(1)}(x_1,x_2,x_3) = \sqrt{\frac{2!}{3!}}[\psi_1(x_1)\psi_1(x_2)\psi_2(x_3)+\psi_1(x_1)\psi_2(x_2)\psi_1(x_3) + \psi_2(x_1)\psi_1(x_2)\psi_1(x_3)]$$

In the second excited state we have one particle in ψ_1 and two in ψ_2

$$E^{(2)} = \varepsilon_1 + 2\varepsilon_2 = \varepsilon_1 + 8\varepsilon_1 = 9\varepsilon_1 = \frac{9\pi^2\hbar^2}{2ma^2}$$

Now, since the value n = 2 occurs twice (two particles are in ψ_2) and n = 1 only, then

$$\psi^{(2)}(x_1,x_2,x_3) = \sqrt{\frac{2!}{3!}}\,[\psi_1(x_1)\psi_2(x_2)\psi_2(x_3) + \psi_2(x_1)\psi_1(x_2)\psi_2(x_3) + \psi_2(x_1)\psi_2(x_2)\psi_1(x_3)$$



(c) If the three particles were identical spin ½ fermions, the ground state corresponds to the case where two particles are in the lowest state ψ_1 (one having a spin-up $|+\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle$, the other with a spin-down $|-\rangle = \left|\frac{1}{2},-\frac{1}{2}\right\rangle$, while the third particle is in the next state ψ_2 (its spin can be either up or down, $|\pm\rangle = \left|\frac{1}{2},\pm\frac{1}{2}\right\rangle$, see the figure above. The ground state energy is

$$E^{(0)} = 2\varepsilon_1 + \varepsilon_2 = 2\varepsilon_1 + 4\varepsilon_1 = 6\varepsilon_1 = \frac{3\hbar^2\pi^2}{ma^2}$$

The ground state wave function is antisymmetric and it is given by

$$\psi^{(0)}(x_1,x_2,x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \psi_2(x_3)\chi(S_3) \end{vmatrix}$$

The first excited state corresponds to one particle in the lowest state ψ_1 (its spin can be either up or down) and the other two particles in the state ψ_2 (the spin of one is up, the other is down.) As in the ground state, the there are also four different ways fo configuring the spins of the three fermions in the first excited state (FES); the FES shown in figure above is just one of the four configurations:

$$\psi^{(1)}(x_1,x_2,x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \psi_2(x_3)\chi(S_3) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \psi_2(x_3)\chi(S_3) \end{vmatrix}$$

These four different states correspond to the same energy,

$$E^{(1)} = \varepsilon_1 + 2\varepsilon_2 = \varepsilon_1 + 8\varepsilon_1 = 9\varepsilon_1 = \frac{9\hbar^2\pi^2}{2ma^2}$$

The excitation energy of the first excited state is $E^{(1)} - E^{(0)} = 9\varepsilon_1 - 6\varepsilon_1 = 3\hbar^2\pi^2/(2ma^2)$

The second excited state corresponds to two particles in the lowest state ψ_1 (one with spin up, the other with spin-down) and the third particle in the third ψ_3 (its spin can be either up or down). This state also has four different spin configurations; hence it is fourfold degenerate:

$$\psi^{(2)}(x_1,x_2,x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_3(x_1)\chi(S_1) & \psi_3(x_2)\chi(S_2) & \psi_3(x_3)\chi(S_3) \end{vmatrix}$$

The energy of the second excited state is

$$E^{(2)} = 2\varepsilon_1 + \varepsilon_3 = 2\varepsilon_1 + 9\varepsilon_1 = 11\varepsilon_1 = \frac{11\hbar^2\pi^2}{2ma^2}$$

The excitation energy of this state is $E^{(2)} - E^{(0)} = 11\varepsilon_1 - 6\varepsilon_1 = 5\varepsilon_1 = 5\hbar^2\pi^2/(2ma^2)$

Problem 2: Consider a system of three noninteracting identical spin ½ particles that are in the same spin sate $\left|\frac{1}{2},\frac{1}{2}\right\rangle$ and confined to move in a one-dimensional infinite potential well of length a: V(x) = 0 for 0 < x < a and V(x) = ∞ for other values of x. Determine the energy and the wave function of the ground state, the first excited state, and the second excited state.

Soln. We may mention first that the single-particle energy and wave function of a particle moving in an infinite well are given by $\varepsilon_n = n^2\hbar^2\pi^2/(2ma^2)$ and $\psi_n(x_i) = \sqrt{2/a}\sin(n\pi x_i/a)$.

The wave function of this system is antisymmetric, since it consists of identical fermions. Moreover, since all the three particles are in the same spin state, no two particles can be in the same state; every energy level is occupied by at most one particle. For instance, the ground state corresponds to the case where the three lowest levels n = 1, 2, 3 are occupied by one particle each. The ground state energy and wave function are thus given by

$$E^{(0)} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \varepsilon_1 + 4\varepsilon_1 + 9\varepsilon_1 = 14\varepsilon_1 = \frac{7\hbar^2\pi^2}{ma^2}$$

$$\psi^{(0)}(x_1,x_2,x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) \\ \psi_2(x_1) & \psi_2(x_2) & \psi_2(x_3) \\ \psi_3(x_1) & \psi_3(x_2) & \psi_3(x_3) \end{vmatrix}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

The first excited state is obtained (from the ground state) by raising the third particle to the fourth level: the levels n = 1, 2 and 4 are occupied by one particle each and the third level is empty:

$$E^{(1)} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \varepsilon_1 + 4\varepsilon_1 + 16\varepsilon_1 = 21\varepsilon_1 = \frac{21\hbar^2\pi^2}{2ma^2}$$

$$\psi^{(1)}(x_1,x_2,x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) \\ \psi_2(x_1) & \psi_2(x_2) & \psi_2(x_3) \\ \psi_4(x_1) & \psi_4(x_2) & \psi_4(x_3) \end{vmatrix}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

In the second excited state, the levels n = 1, 3, 4 are occupied by one particle each; the second level is empty

$$E^{(2)} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \varepsilon_1 + 9\varepsilon_1 + 16\varepsilon_1 = 26\varepsilon_1 = \frac{13\hbar^2\pi^2}{ma^2}$$

$$\psi^{(2)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) \\ \psi_3(x_1) & \psi_3(x_2) & \psi_3(x_3) \\ \psi_4(x_1) & \psi_4(x_2) & \psi_4(x_3) \end{vmatrix} \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

Problems on Identical particles

1. Three imaginary 'spinless' fermions are confined to a 1– D box of length L the confinement potential is

$$V = \begin{cases} 0 & 0 \le x < L \\ \infty & \text{otherwise} \end{cases}$$

what is the ground state of the system? also find the state of the system.

2. If the particles are electrons in the above problem, what is the energy?

3. Consider a system of three non-interacting, identical spin $\frac{1}{2}$ particles that are in the same spin state $\left|\frac{1}{2}, \frac{1}{2}\right\rangle$ and confined to move in a 1–D infinite potential well of length 'a'. $V(x) = 0$ for $0 < x < a$ and $V(x) = \alpha$ for other values of x. Determine the energy and wave function of the ground state and the first excited state.

4. Consider an election of mass 'm' and spin 1/2 in a 3 – D box of length L :

$$V(\vec{r}) = \begin{cases} 0, & \text{inside the box where } 0 < x < L \\ \infty, & \text{outside} \qquad\quad 0 < y < L \\ & \qquad\qquad\quad 0 < z < L \end{cases}$$

(a) compute the energy eigen functions and eigen values of the electron.
(b) What are the degeneracies of the lowest two energy levels?
(c) Suppose we put three electrons in this box. Assuming that the electrons are non-interacting, what is the degeneracy of the lowest energy level?

5. Consider the Hamiltonian, H, of a free particle of mass 'm' moving on a circle of radius a discribed by the angle θ.

$$H = -\frac{\hbar^2}{2ma^2}\frac{\partial^2}{\partial\theta^2}$$

consider the time independent Schriodinger eq^n $H\psi_E(\theta) = E\psi_E(\theta)$
(a) what boundary condition should be imposed on $\psi_E(\theta)$?
(b) compute the eigen energies and corresponding normalized eigen functions
(c) Is there any. degeneracy in the eigen value? Explain.

UNIT - VII
SCATTERING THEORY

Quantum Scattering theory

In QST we imagine an incident plane wave $\psi(z) = Ae^{ikz}$, travelling in the z-direction, which encounters a scattering potential, producing an outgoing spherical wave. We look for solution to the Schriodenger equation of the general form.

$$\psi(r,\theta) \approx A\left\{\theta e^{ikz} + f(\theta)\frac{e^{ikr}}{r}\right\} \text{ for large } r \quad \rightarrow (1)$$

The whole problem is to determine the scattering amplitude $f(\theta)$, which gives us the probability of scattering in a given direction θ.

The probability that the incident particle, travelling at speed v, passes through the infinitesimal area $d\sigma$, in time dt, is

$$dp = |\psi_{incident}|^2 dv = |A|^2 (vdt)\, df.$$

Hence, but this must be equal to the probability that the particle scatters into the corresponding solid angle $d_p = |\psi_{scattered}|^2 dv = \frac{|A|^2 |f(\theta)|^2}{r^2}(vdt) r^1 d\Omega$. Hence $D(\theta) = \frac{d\sigma}{d\Omega} = |f(\theta)|^2$

Partial wave analysis :

This method is based upon expansion of $\psi(\vec{r})$ in terms of angular momentum eigen function. It is applicable if the potential is spherically symmetric. The new expansion must of course be consistent with the asymptotic form (1). When this requirement is imposed, one gets a formal expression for the scattering amplitude as as infinite series; each term of the series is the contribution to $f(\theta,)$ from a partial wave characterized by a particular angular momentum. The first few terms in the series approximated $f(\theta,\theta)$ If The Incident Particle is of low energy. Thus the partial wave method leads to a low energy approximation.

We know, the schriodinger equation for a spherically symmetrical potential $v(r)$ admits the separable solutions

$$\psi(r,\theta,\phi) = R(r)\, Y_i^m(\theta,\phi)$$

where Y_i^m is a spherical harmonic, and $\mu(r) = rR(r)$ satisfies the radial equation

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{L(L+1)}{r^2}\right]u = Eu$$

At very large r the potetial goes to zero, and the centrifugal contribution is negligible, so

$$\frac{d^2u}{dr^2} \approx -k^2 u$$

$$\Rightarrow \quad u(r) = c.e^{ikr} + d\, e^{-ikr}$$

For the scattered wave, evidently D=0, At very large r, then,

$$\boxed{R(r) \sim \frac{e^{ikr}}{r}}$$

In the intermediate rigion (where v can be ignored but the centrifugal term cannot l, the radial equation becomes

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u = -k^2 u$$

The general solution is a linear combination of spherical Bessel functions:

$$u(r) = A\, rJ_i(kr) + B\, n_i(kr)$$

However neither j_i nor n_i represents an outgoing wave. What we need are the linear combinations analogous to e^{ikr}, and e^{-ikr}, these are known as spherical Hankel functions. We find that we need spherical Hankel function of the first kind:

$R(r) \sim h_l^{(1)}(kr)$

Thus the exact wave function, outside the scattering region (where $v(r) = 0$, is

$$y(r, \theta, \phi) = A\left\{e^{ikz} + \sum_{l,m} c_{l,m} h_l^{(1)}(kr) y_l^m(\theta, \phi)\right\}$$

As the potential is sperically symmetric. The wave function cannot depends on ϕ.

$$\text{Hence, } \psi(r,\theta) = A\left\{e^{ikz} + k\sum_{l=0}^{\infty} i^{l+1}(2l+1) a_l h_l^{(1)}(kr) p_l(\cos\theta)\right\}$$

$$\text{For very large } r, \ \psi(r,\theta) = A\left\{e^{ikz} + f(\theta)\frac{e^{ikr}}{r}\right\}$$

where $\boxed{f(\theta) = \sum_{l=0}^{\infty}(2l+1) a_l p_l(\cos\theta)}$, a_l is called the the partial wave amplitude.

The differential Scattering cross-section is

$$D(\theta) = |f(\theta)|^2 = \sum_{l} \sum_{l'} (2l+1)(2l^1+1) a_{l'}^{*}\, a_l, P_l(\cos\theta) P_{l'}(\cos\theta)$$

And the total cross-section is

$$s = 3\pi \sum_{i=0}^{\alpha} (2i+1)|a_i|^2$$

The scattering amplitude, in terms of phase shifts:

e^{ikz} satisfies the Schrodinger equation with $v = 0$. on the other hand, we have seen that the genral solution to the Schrodinger equation with $v = 0$ can be written in the form.

$$\sum_{l,m} [A_{lm}\, j_l(kr) + B_{lm}\, n_l(kr)] y_l^m(\theta, \phi)$$

But e^{ikz} is finite at the origin. And $z = r\cos\theta$ no ϕ dependence so only $m = 0$ terms occur.

$$e^{ikz} = \sum_{i=0}^{\alpha} i^l (2l+1) j_i(kr) P_l(\cos\theta)$$

Using this, we can write

$$\boxed{\psi(r,\theta) = A\sum_{l=0}^{\infty} i^l (2l+1)\left[j_l(kr) + ika_l h_l^{(1)}(kr)\right] P_l(\cos\theta)}$$

Because the angular momentum is conserved, each partial wave scatters independently with no change in amplitude, only in phase.

The effect of potential on the partial waves in the asymptotic region is simply to change the phase of the partial wave. The whole theory of scattering is just reduced to the problem of calculating the phase shift δ, for a specified potential.

It can be shown,

$$\boxed{f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1) e^{i\delta l} \sin(\delta_l) P_l(\cos\theta)} \qquad \boxed{\sigma = \frac{4\pi}{k^2}\sum_{i=0}^{\infty}(2l+1)\sin^2\delta_l}$$

Optical Theorem $\boxed{\sigma = \frac{4\pi}{k}\,\mathrm{Im} f(0)}$

relates the total cross- section to the inaginary part of the forward (θ=0) scattering amplitude.

Proof

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1) e^{i\delta l} \sin(\delta_l) P_l(\cos\theta)$$

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\alpha}(2l+1) e^{i\delta l} \sin(\delta_l)$$

$P_l(1) = 1$

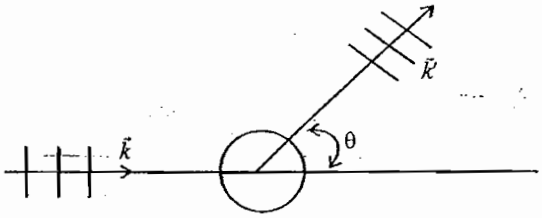
$$Imf(0) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta l$$

Thus, $$= \boxed{\sigma = \frac{4\pi}{k}\,\mathrm{Im}\, f(0)}$$

Quantum theory of scattering

The Born approximation

In the Born approximation, incident and scatterd particles are in plane wave states.



Domain of Interaction

In this approximation, the pertubation Hamiltonian is the interaction potential which can be viewed as being. 'turned on' during the time that the incident particle is in the range of the potential. The incident particle enters the range of interaction with momentum $\hbar\vec{k}$ and leaves the range of interaction with momentum $\hbar\vec{k}$.

Let us suppose that the scattering experiment is performed in a large cubical box of volume L^3. Normalized plane wave states corresponding to $\vec{k}$ and $\vec{k}'$ are then given by

$$|\vec{k}> = \frac{e^{i\vec{k}\cdot\vec{r}}}{L^{3/2}},\ |\vec{k}'> = \frac{e^{i\vec{k}'\vec{r}}}{L^{3/2}}$$

The rate of transition from the $\vec{k}$ to the $\vec{k}'$ state, caused by the perturbing potential $v(r)$

$$T_{kk'} = \frac{2\hbar}{\hbar}|<k'|v|k>|^2\, P(E_{k'})$$

As the experiment is performed in a large box of volume L^3, we may write $P(E_{k'}) = \frac{mL^3k'}{2\pi^2\hbar^2}$

The no. of particles scattered into $d\Omega$ per second is $J_{inc}\, d\sigma$

We note that the incident plane wave $|\vec{k}>$ corresponds to an incident current

$$J_{inc} = \frac{\hbar\vec{k}}{mL^3}$$

Now $P(E_k)$ is isotropic in k', it represents the density of final $\vec{k}'$ states in all 4π solid angle. to select those scattered states that lie in the direction $d\Omega$ about $\vec{k}'$, we multiply $P(E_k')$ by the ratio $\frac{d\Omega}{4\pi}$.

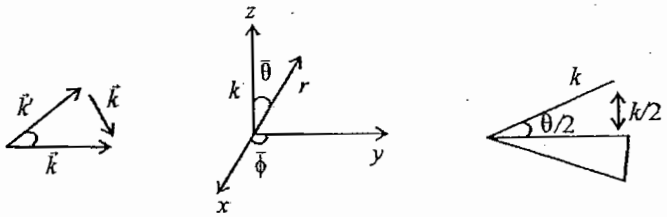
$$\text{Thus, } J_{inc}\, dv = \frac{d\Omega}{4\hbar}\lceil kk' \ ;\ \frac{d\sigma}{d\Omega} = \left(\frac{mL^3}{2\hbar\hbar^2}\right)\frac{k'}{k}|<k'|v|k>|^2$$

Since the particles suffer no loss in energy in the scattering process, we may equate $k = k'$

Scattering Amplitude:

Now, $\frac{d\sigma}{d\Omega} = |f(\theta)|^2$ $\qquad \boxed{f(\theta) = -\frac{m}{2\pi\hbar^2}\int v(r)e^{i\vec{r}(\vec{k}-\vec{k}')}d\vec{r}}$

This formula for the scattering amplitude may be further simplified through the substitution



$\vec{k} = \vec{k} - \vec{k}'$

As, $|\vec{k}| = |\vec{k}'|$, we may set $k = 2k \sin\left(\frac{\theta}{2}\right)$

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\bar{\theta}\, d\bar{\theta} \int_0^{\infty} r^2 dr\ V(r) e^{ikr\cos\bar{\theta}} = -\frac{m}{\hbar^2}\int_0^{\infty} r^2 dr\, v(r) \int_{-1}^{1} d\eta\, e^{ikr\eta} \qquad \eta = \cos\bar{\theta}$$

$$\boxed{f(\theta) = -\frac{2m}{\hbar^2 k}\int_0^{\infty} dr\ r\ v(r)\sin kr}$$

This expression for the scattering amplitude is called the standard form of the Born approximation. One should note that this formula is derived on the basis of perturbation theory according to which The scattering potential should be small compared to the free particle (unperturbed) Hamiltonian. This will be case for Sufficiently large incident energies or
Sufficiently weak strenths of potential
Validity of 1st Born approximation (mathematical form)

$$\boxed{\frac{m}{\hbar^2 k}\left|\int_0^{\infty} v(r')\left(e^{ikr'} - 1\right) dr'\right| << 1}$$

Problems on Scattering:

1. Using the Born approximation, evaluate the differential scattering cross-section for scattering particles of man m and incident energy E by the repulsive spherical well with potential

$$v(r) = \begin{cases} v_0, & o < r < a \\ 0. & r > a \end{cases}$$

2. Show that for a spherically symmetric potential $v(r) = g\,\delta(r)$ where $\delta(r)$ is a 3-D δ-function, and g is a constant, the Born approximation gives a scattering amplitude.

$$f(\theta) = -\frac{m}{2\pi\hbar^2} g$$

3. Calculate the scattering amplitude and differential cross-section for scattering from the Yukawa potential

$$v(r) \quad = c\frac{e^{-\mu r}}{r}$$

4. Derive the Rutherford scattering cross-section from quantum mechanics

Solutions:

(1) We have, $f(\theta) = -\frac{2m}{\hbar^2 k}\int_0^{\infty} dr\, r v(r)\sin kr$

Now, in the given problem

$$f(\theta) = -\frac{2m\,v_0}{\hbar^2 k}\int_0^{\infty} r\sin(kr)dr = -\frac{2m\,v_0}{\hbar^2 k}\left[-\frac{r\cos kr}{k}\Big|_0^a + \int_0^a \cos kr\, dr\right] = -\frac{2m\,v_0}{\hbar^2 k}\left[-\frac{1}{k}a\cos ka + \frac{1}{k^2}\sin ka\right]$$

$$= -\frac{2m\,v_0}{\hbar^2 k}\left[\frac{\sin(ka)}{k^2} - \frac{a\cos ka}{k}\right]$$

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 \qquad k = 2k\sin(\theta/2)$$

Where $\boxed{k = 2\sqrt{\frac{2mE}{\hbar^2}}\sin(\theta/2)}$

(2) $f(\theta) = -\frac{m}{2\pi h^2}\int v(r)\, e^{i\vec{r}.(\vec{k}-\vec{k}')}dr = -\frac{m}{2\pi h^2}\int g\,\delta(r)\, e^{i\vec{k}.\vec{r}}dr \quad \Rightarrow \quad \boxed{f(\theta) = \frac{-mg}{2\hbar\hbar^2}}$

(3) $v(r) = C\frac{e^{-\mu r}}{r} \quad \Rightarrow f(\theta) = \frac{m}{2\pi\hbar^2}\int v(r) e^{i\vec{k}.\vec{r}}d\vec{r} = -\frac{2m}{\hbar^2 k}\int_0^\infty dr\, r\, v(r)\sin kr = -\frac{2m}{\hbar^2 k}\int_0^\infty e^{-\mu r}\sin(kr)\,dr$

$$= \int_0^\infty e^{-\mu r}\sin(kr)\,dr = \frac{k}{\mu^2 + k^2}$$

Thus, $f(\theta) = \frac{2mc}{\hbar^2}\frac{1}{\mu^2 + k^2}$

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{4m^2c^2}{\hbar^4}\frac{1}{\left(\mu^2 + k^2\right)^2}}$$

(4) Here, $v(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$

From the above problem, put m = 0, $c = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$

$$f(\theta) = -\frac{2m q_1 q_2}{4\pi\varepsilon_0\hbar^2}\frac{1}{k^2}$$

Use $k = 2k\sin\theta/2 = 2\sqrt{\frac{2mE}{\hbar^2}}\sin\theta/2$

$$\boxed{f(\theta) = \frac{q_1 q_2}{16\pi\varepsilon_0}\frac{1}{E\sin^2\theta/2}} \qquad \text{Thus,} \qquad \boxed{\frac{d\sigma}{d\Omega} = \left(\frac{q_1 q_2}{16\pi\varepsilon_0}\right)^2\frac{1}{E^2\sin^4\theta/2}}$$

UNIT-VIII

TIME INDEPENDENT PERTURBATION THEORY

In quantum mechanics most problems cannot be solved exactly. Exact solutions of the schrodinger equation exist only for one particle system or a few idealized systems. To solve general problems, one must resort to approximation methods. There are various methods of approximation and each has its own area of applicability. As perturbation theory, variational method, and the WKB method.

Perturbation Thoery: Perturbation theory is one of the approximation methods to solve the Schrodinger equation. Perturbation theory is of two types.

1. **Stationary (time independent) Pertubation theory**
In this perturbation theory Hamiltonian does not depend on time explicitly. The stationary perturbation theory is concerned with finding the changes in energy levels and eigen functions of a system when a small perturbation is applied. Perturbation theory is based on the assumptions that problem we wish to solve is , only slightly different from a problem that can be solved exactly.

2. **Time dependent perturbation theory**: If Hamiltonian depends on time explicitly then perturbation theory is called time dependent perturbation theory.

Time independent perturbation theory: This method is most suitable when total Hamiltonian is very close to unperturbed Hamiltonian.

$$\hat{H} = \hat{H}_0 + \hat{H}_p$$

$\hat{H}_0$ Unperturbed Hamiltonian is time independent for which Schrodinger equation is exactly solvable.

$\hat{H}_p$ Perturbed Hamiltonian time independent may be constant or it may be a function of both the space and momentum co-ordinates $\hat{H}_p$ is very small in comparision to $\hat{H}_0$, its effect on energy levels and wavefunction will be small.

There are two cases depending on whether the exact solution of $\hat{H}_0$ are degenerate or non-degenerate.

NONDEGENERATE TIME INDEPENDENT PERTURBATION THEORY

In this case $\hat{H}_0$ has nondegenrate eigenvalues, that is for every energy $E_n^{(0)}$ there corresponds only one eigenstate $|\phi_n\rangle$

$$\hat{H}_0 |\phi_n\rangle = E_n^0 |\phi_n\rangle \qquad \ldots (1)$$

Let $\hat{H}_p = \lambda \hat{H}'$ where $\lambda (<<1)$ dimensionless real parameter.

First order correction in energy: $E_n^1 = \langle \phi_n | \hat{H}_p | \phi_n \rangle$ ....(2)

It is the expectation value of perturbed Hamiltonian over unperturbed state.

Energy correct upto Ist order perturbation

$$E_n = E_n^{(0)} + E_n^{(1)} = E_n^{(0)} + \langle \phi_n | \hat{H}_p | \phi_n \rangle \qquad \ldots (3)$$

Note that for some systems, the first order correction E_n^1 vanishes exactly. In such cases, one needs to consider higher-order terms.

First order correction in wave function

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{<\phi_m|\hat{H}_p|\phi_n>}{E_n^{(0)} - E_m^{(0)}} |\phi_m> \quad \ldots (4)$$

Wave function correct upto first order.

$$|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} \frac{\langle\phi_m|\hat{H}_p|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}} |\phi_m\rangle \quad \ldots (5)$$

Second order correction in energy : $E_n^{(2)} = \sum_{m\neq n} \frac{|\langle\phi_m|\hat{H}_p|\phi_n>|^2}{E_n^{(0)} - E_m^{(0)}}$ ...(6)

Energy correct upto second order

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = E^{(0)} + \langle\phi_n|\hat{H}_p|\phi_n\rangle + \sum_{m\neq n} \frac{|\langle\phi_m|\hat{H}_p|\phi_n\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad \ldots (7)$$

Validity of the time independent perturbation theory expansion parameter must be small

$$\frac{\langle\phi_m|\hat{H}_p|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}} << 1$$

Note: In case of Schrodinger Harmonic oscillator the first order correction in energy is zero if the perturbation is proportional to odd power of x.

Problem: If the perturbation $H' = ax$ where 'a' is a constant, is added to infinite square well potential.

$$V(x) = \begin{cases} 0, & \text{for } 0 < x < \pi \\ \infty, & \text{otherwise} \end{cases}$$

The first order correction to ground state energy is

(a) $\frac{a\pi}{2}$ (b) $a\pi$ (c) $\frac{a\pi}{4}$ (d) $\frac{a\pi}{\sqrt{2}}$

Soln. $H' = ax \Rightarrow E_n^{(1)} = \int_0^\pi \psi_n^0 H' \psi_n^0 dx$ where, $\psi_n(x) = \sqrt{\frac{2}{\pi}} \sin\frac{n\pi x}{\pi}$

$$E_n^1 = \int_0^\pi ax \frac{2}{\pi} \sin^2\frac{n\pi x}{\pi} dx = \frac{2}{\pi} a \int_0^\pi \frac{x}{2}\left[1 - \cos\frac{2n\pi x}{\pi}\right] dx = \frac{a}{\pi}\int_0^\pi (x - x\cos 2nx) dx$$

$$= \frac{a}{\pi}\left[\frac{x^2}{2} - x\frac{\sin 2nx}{2n} - \frac{\cos 2nx}{(2n)^2}\right]_0^\pi = \frac{a}{\pi}\left[\frac{\pi^2}{2} - 0 - \frac{1}{4n^2}\{\cos 2n\pi - \cos 0\}\right]$$

$$= \frac{a}{\pi}\left[\frac{\pi^2}{2} - 0 - \frac{1}{4n^2}(1-1)\right] = \frac{a}{\pi}\left[\frac{\pi^2}{2} - 0\right] \Rightarrow E_n^{(1)} = \frac{a\pi}{2}$$

Problem: A particle of mass 'm' is confined in a infinite potential well.

$$V(x)=\begin{cases}0, & \text{for } 0<x<L\\ \infty, & \text{otherwise}\end{cases}$$

It is subjected to a perturbing potential $V_p(x)=V_0\sin\left(\frac{2\pi x}{L}\right)$ within the well.

What is the correction to the ground state energy in the first order?

Soln. $$E_n^{(1)}=\frac{2V_0}{L}\int_0^L \sin^2\frac{\pi x}{L}\sin\frac{2\pi x}{L}dx=\frac{2V_0}{L}\int_0^L \sin\frac{2\pi x}{L}\frac{1}{2}\left[1-\frac{\cos 2\pi x}{L}\right]dx$$

$$=\frac{V_0}{L}\int_0^L\left(\sin\frac{2\pi x}{L}-\sin\frac{2\pi x}{L}\cos\frac{2\pi x}{L}\right)dx$$

$$=\frac{V_0}{L}\left[-\frac{\cos\frac{2\pi x}{L}}{\frac{2\pi}{L}}-0\right]_0^L=\frac{V_0}{L}\frac{L}{2\pi}[\cos 2\pi-\cos 0]=\frac{V_0}{2\pi}[1-1]=0$$

Problem: A particle of charge q and mass m, which is moving in a one-dimensional harmonic potential of frequency ω, is subject to a weak electric fields. Calculate the energy to first non zero correction.

Soln. Total Hamiltonian is given by

$$\hat{H}=\hat{H}_0+\hat{H}_p=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2\hat{x}^2+qE\hat{x} \qquad \ldots (1)$$

$$\hat{H}_p=qE\hat{x} \qquad \ldots (2)$$

First order correction to energy

$$E_n^{(1)}=<\phi_n|\hat{H}_p|\phi_n>=<\phi_n|qE\hat{x}|\phi_n>=qE<\phi_n|\hat{x}|\phi_n>=0$$

Second order correction to energy

$$E_n^{(2)}=\sum_{m\neq n}\frac{\left|\langle\phi_m|\hat{H}_p|\phi_n\rangle\right|^2}{E_n^{(0)}-E_m^{(0)}}=\sum_{m\neq n}\frac{\left|\langle\phi_m|qE\hat{x}|\phi_n\rangle\right|^2}{E_n^{(0)}-E_m^{(0)}}=q^2E^2\sum_{m\neq n}\frac{\left|\langle\phi_m|\hat{x}|\phi_n\rangle\right|^2}{E_n^{(0)}-E_m^{(0)}}$$

$$=q^2E^2\sum_{m\neq n}\frac{\left|\left\langle\phi_m\left|\left(\sqrt{\frac{\hbar}{2m\omega}}\,\hat{a}^\dagger+\sqrt{\frac{\hbar}{2m\omega}}\,\hat{a}\right)\right|\phi_n\right\rangle\right|}{E_n^{(0)}-E_m^{(0)}}$$

$$=q^2E^2\sum_{m\neq n}\frac{|<\phi_m|\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n+1}\,|\phi_{n+1}>+<\phi_m|\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n}\,|\phi_{n-1}>|}{E_n^{(0)}-E_m^{(0)}}$$

$$=g^2E^2\left[\frac{|<\phi_{n+1}|\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n+1}\,|\phi_{n+1}>|^2}{E_n^{(0)}-E_m^{(0)}}+\frac{|<\phi_{n-1}|\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n}\,|\phi_{n-1}}{E_n^{(0)}-E_{n+1}^{(0)}}\right]$$

$$= q^2E^2\left[\frac{(n+1)\frac{\hbar}{2m\omega}}{\hbar\omega} + \frac{n\frac{\hbar}{2m\omega}}{\hbar\omega}\right] \Rightarrow E_n^{(2)} = \frac{-q^2E^2}{2m\omega^2}$$

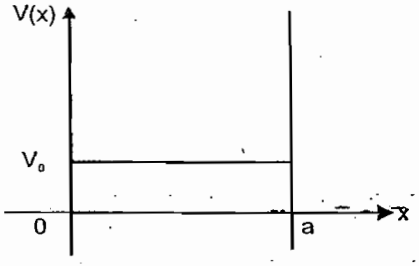
Energy correct upto first nonzero correction

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \Rightarrow E_n = \left(n+\frac{1}{2}\right)\hbar\omega - \frac{q^2E^2}{2m\omega^2}$$

Problem: The unperturbed wave function for the infinite square well are

$$\psi_n^0(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

(a) Suppose we perturb the system by simply raising the floor of the well a constant amount V_0 in the figure. Find the first-order correction to the energies.

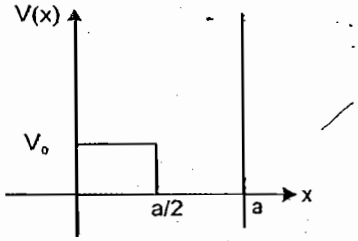


Soln. First-order correction to the energy of the nth state is

$$E_n^1 = \left\langle \psi_n^{(0)} \mid V_0 \mid \psi_n^{(0)} \right\rangle = V_0 \left\langle \psi_n^{(0)} \mid \psi_n^{(0)} \right\rangle = V_0$$

The energy correct upto first order, $E_n = E^{(0)} + E^{(1)} = \frac{\pi^2\hbar^2n^2}{2ma^2} + V_0$

(b) If the perturbation extends only half way across the well (figure.)



$$E_n^{(1)} = \int_0^{a/2} \psi_n^{(0)}(x) V_0 \psi_n^{(0)}(x)\, dx = V_0 \int_0^{a/2} \left(\frac{2}{a}\right)\sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{2V_0}{a}\int_0^{a/2} \frac{\left(1-\cos\frac{2n\pi x}{a}\right)}{2} dx = \frac{2V_0}{2a}\left[x - \frac{\sin\frac{2n\pi x}{a}}{\frac{2n\pi x}{a}}\right]_0^{\frac{a}{2}} = \frac{V_0}{2} - 0 = \frac{V_0}{2}$$

Energy correction upto first order

$$E_n = E_n^0 + \frac{V_0}{2} = \frac{n^2\hbar^2\pi^2}{2ma^2} + \frac{V_0}{2}$$

Problem: A quantum harmonic oscillator is in the energy eigenstate $|n\rangle$. A time independent perturbation $\lambda\left(\hat{a}^{\dagger}\hat{a}\right)^2$ acts on the particle, where λ is a constant of suitable dimensions and $\hat{a}$ and $\hat{a}^{\dagger}$ are lowering and raising operators respectively. Then the first order energy shift is given by

(a) λn (b) $\lambda^2 n$ (c) λn^2 (d) $(\lambda n)^2$

Soln. **(c)**

Problem: Let $E_n'(n = 0,1,2,.....)$ be the energy eigenvalues for a particle of mass m placed in an anharmonic potential $V(x) = \frac{1}{2}m\omega^2x^2 + ax^4 (a > 0)$. Let $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$. Then according to the first order perturbation theory.

(a) $E_0' = E_0$ (b) $E_0' > E_0$ (c) $E_0' < E_0$ (d) $E_n' < E_n$ for all n

Soln. **(b)** $E_0' > E_0$

Problem: Calculate the energy of the nth excited state to first order perturbation theory for a spinless particle of mass m moving in an infinite well of length 2L, with walls at x = 0 and x = 2L

$$V(x) = \begin{cases} 0 & 0 \le x \le 2L \\ \infty & \text{otherwise} \end{cases}$$

Which is modified at the bottom by the following perturbations

(a) $V_p(x) = \lambda V_0 \sin\left(\frac{\pi x}{2L}\right)$ (b) $V_p(x) = \lambda V_0 \delta(x - L)$ where $\lambda << 1$

Soln. **(a)** The exact energy and wave functions for this well is given by

$$E_n = \frac{n^2\hbar^2\pi^2}{2m(2L)^2} = \frac{n^2\hbar^2\pi^2}{8mL^2}, \quad \phi_n(x) = \sqrt{\frac{2}{2L}}\sin\left(\frac{n\pi x}{2L}\right) = \sqrt{\frac{1}{L}}\sin\left(\frac{n\pi x}{2L}\right)$$

First order energy correction, $\hat{H}_p = V_p = \lambda V_o \sin\left(\frac{\pi x}{2L}\right)$

$$E_n^{(1)} = \langle \phi_n | \hat{H}_p | \phi_n \rangle = \frac{1}{L}\int_0^{2L} \sin^2\left(\frac{n\pi x}{2L}\right)\lambda V_0 \sin\left(\frac{\pi x}{2L}\right)dx = \frac{\lambda V_0}{L}\int_0^{2L} \sin^2\left(\frac{n\pi x}{2L}\right)\sin\left(\frac{\pi x}{2L}\right)dx$$

$$= \frac{\lambda V_0}{L}\left[\int_0^{2L}\left(\frac{1-\cos\frac{2n\pi x}{2L}}{2}\right)\sin\left(\frac{\pi x}{2L}\right)dx\right] = \frac{\lambda V_0}{2L}\int_0^{2L}\left[\sin\left(\frac{\pi x}{2L}\right) - \cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{\pi x}{2L}\right)\right]dx$$

$$= \frac{\lambda V_0}{2L}\int_0^{2L}\left[\sin\left(\frac{\pi x}{2L}\right) - \sin\frac{(2n+1)\pi x}{2L} + \frac{\sin(2n-1)\pi x}{2L}\right]dx$$

$$= \frac{\lambda V_0}{2L}\left[\frac{-\cos\left(\frac{\pi x}{2L}\right)}{\frac{\pi}{2L}} + \cos\frac{(2n+1)\pi x}{2L} - \frac{\cos\frac{(2n-1)\pi x}{2L}}{(2n-1)\frac{\pi}{2L}}\right]_0^{2L}$$

$$= \frac{\lambda V_0}{\pi}\left[1+1+\frac{(2n-1)[\cos(2n+1)\pi-1]-(2n+1)[\cos(2n-1)\pi-1]}{(4n^2-1)}\right]$$

$$= \frac{\lambda V_0}{\pi}\left[2\times\frac{4n^2-2-2n+2n-2n+2n+1+1}{(4n^2-1)}\right] \quad \Rightarrow \quad E^1 = \frac{2\lambda V_0}{\pi}\frac{4n^2}{4n^2-1}$$

Energy correct upto first order $E_n = E_n^{(0)} + E_n^{(1)} = \frac{n^2\hbar\pi^2}{8mL^2} + \frac{2\lambda V_0}{\pi}\frac{4n^2}{4n^2-1}$

(b) $\hat{H}_p = \lambda V_0 \delta(x-L)$

$$E_n^1 = \frac{1}{L}\int_0^{2L}\sin^2\left(\frac{n\pi x}{2L}\right)\lambda V_0\delta(x-L)dx$$

$$\int_{x_1}^{x_2} f(x)\delta(x-a) = f(a) \quad \text{if } x_1 < a < x_2$$
$$= 0 \quad \text{otherwise}$$

$$= \frac{\lambda V_0}{L}\int_0^{2L}\sin^2\left(\frac{n\pi x}{2L}\right)\delta(x-L)dx = \frac{\lambda V_0}{L}\sin^2\left(\frac{n\pi}{2}\right) \quad \Rightarrow E_n = \frac{n^2\hbar\pi^2}{8mL^2} + \frac{\lambda V_0}{L}\sin^2\left(\frac{n\pi}{2}\right)$$

Exercise:

Problem: An unperturbed two-level system has energy eigenvalues E_1 and E_2 and eigenfunctions $\begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$. When perturbed its Hamiltonian is represented by $\begin{bmatrix}E_1 & A\\ A^* & E_2\end{bmatrix}$

(1) The first order correction to E_1 is

(a) 4A (b) 2A (c) A (d) 0

(2) The second order correction to E_1 is

(a) 0 (b) A (c) $\frac{A^2}{E_2-E_1}$ (d) $\frac{A^2}{E_1-E_2}$

(3) The first order correction to wave function $\begin{pmatrix}1\\0\end{pmatrix}$

(a) $\begin{bmatrix}0\\ \frac{A^*}{E_1-E_2}\end{bmatrix}$ (b) $\begin{bmatrix}0\\1\end{bmatrix}$ (c) $\begin{bmatrix}\frac{A^*}{E_1-E_2}\\ 0\end{bmatrix}$ (d) $\begin{bmatrix}1\\1\end{bmatrix}$

Soln. $\hat{H} = \hat{H}_0 + \hat{H}_p = \begin{bmatrix}E_1 & 0\\ 0 & E_2\end{bmatrix} + \begin{bmatrix}0 & A\\ A^* & 0\end{bmatrix} \Rightarrow \hat{H}_p = \begin{bmatrix}0 & A\\ A^* & 0\end{bmatrix} \quad |\phi_{n_1}\rangle = \begin{bmatrix}1\\0\end{bmatrix}$

(1) $E_1^{(1)} = \langle\phi_{n_1}|\hat{H}_p|\phi_{n_1}\rangle = [1\ 0]\begin{bmatrix}0 & A\\ A^* & 0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = [1\ 0]\begin{bmatrix}0 & A\\ A^* & 0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = 0$

(2) $E_1^{(2)} = \sum_{m\neq n}\frac{|\langle\phi_m|\hat{H}_p|\phi_n\rangle|^2}{E_n-E_m} = \frac{|\langle\phi_{n_2}|\hat{H}_p|\phi_{n_1}\rangle|^2}{E_1-E_2}$

$\langle\phi_{n_2}|\hat{H}_p|\phi_{n_1}\rangle = [0\ 1]\begin{bmatrix}0 & A\\ A^* & 0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = A^* \Rightarrow E_1^2 = \frac{|A^*|^2}{(E_1-E_2)}$

$$(3)|\phi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle \phi_{n_2}|\hat{H}_p|\phi_{n_1}\rangle|\phi_{n_2}\rangle}{E_1 - E_2} = \begin{pmatrix} A^* \\ E_1 - E_2 \end{pmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{pmatrix} 0 \\ \frac{A^*}{E_1 - E_2} \end{pmatrix}$$

Problem: Consider a system whose Hamiltonian is given by

$$\hat{H} = E_0 \begin{bmatrix} 1+\lambda & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 \\ 0 & 0 & 3 & -2\lambda \\ 0 & 0 & -2\lambda & 7 \end{bmatrix} \quad \text{where } \lambda << 1$$

(a) By decomposing this Hamiltonian into $\hat{H} = \hat{H}_0 + \hat{H}_p$, find the eigenvalues and eigenstates of the unperturbed Hamiltonian $\hat{H}$.

(b) Using first and second order non-degenerate perturbation theory. Find the energy correction to second order and eigenstates to first order.

Soln. **(a)** $$\hat{H} = \hat{H}_0 + \hat{H}_p = E_0 \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 7 \end{bmatrix} + E_0 \begin{bmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{bmatrix}$$

$\hat{H}_0$ is diagonal so, its exact eigenvalues $E_1^{(0)} = E_0$, $E_2^{(0)} = 8E_0$, $E_3^{(0)} = 3E_0$, $E_4^{(0)} = 7E_0$

Exact eigenfunction, $|\phi_1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$ $|\phi_2\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}$ $|\phi_3\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}$ $|\phi_4\rangle = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$

(b) First order correction to

$$E_1^{(1)} = \langle \phi_1|\hat{H}_p|\phi_1\rangle = \begin{bmatrix} 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \lambda E_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda E_0 \\ 0 & 0 & -2\lambda E_0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \lambda E_0$$

First order correction to $E_2^{(1)} = 0 = \langle \phi_2|\hat{H}_p|\phi_2\rangle$

to $E_3^{(1)} = 0 = \langle \phi_3|\hat{H}_p|\phi_3\rangle$

to $E_4^{(1)} = 0 = \langle \phi_4|\hat{H}_p|\phi_4\rangle$

Second order perturbation to $E_1^{(2)} = \sum_{m\neq n} \frac{|\langle \phi_m|\hat{H}_p|\phi_n\rangle|^2}{E_1^{(0)} - E_m^{(0)}}$

$$= \frac{|<\phi_2|\hat{H}_p|\phi_1>|^2}{E_1^{(0)}-E_2^{(0)}} + \frac{|<\phi_3|\hat{H}_p|\phi_1>|^2}{E_1^{(0)}-E_3^{(0)}} + \frac{|<\phi_4|\hat{H}_p|}{E_1^{(0)}-E_4^{(0)}} = 0$$

$$<\phi_2|\hat{H}_p|\phi_1> = <\phi_3|\hat{H}_p|\phi_1> = <\phi_4|\hat{H}_p|\phi_1> = 0; \qquad E_2^{(2)} = \sum_{m=1,3,4} \frac{|<\phi_m|\hat{H}_p|\phi_2|^2}{E_2^{(0)}-E_m^{(0)}} = 0$$

$$E_3^{(2)} = \sum_{m=1,3,4} \frac{|\langle\phi_m|\hat{H}_p|\phi_2\rangle|^2}{E_3^{(0)}-E_m^{(0)}} = \frac{|\langle\phi_1|\hat{H}_p|\phi_3\rangle|^2}{E_3^{(0)}-E_1^{(0)}} + \frac{|\langle\phi_2|\hat{H}_p|\phi_3\rangle|^2}{E_3^{(0)}-E_2^{(0)}} + \frac{|\langle\phi_4|\hat{H}_p\phi\rangle|}{E_3^{(0)}-E_4^{(0)}} = 0+0+\frac{|<\phi_4|\hat{H}_p|\phi_3>|^2}{(3-7)E_0}$$

$$\Rightarrow \langle\phi_3|\hat{H}_p|\phi_4\rangle = \langle\phi_4|\hat{H}_p|\phi_3\rangle = [0\ 0\ 0\ 1]\begin{bmatrix}\lambda E_0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & -2\lambda E_0\\ 0 & 0 & -2\lambda E_0 & 0\end{bmatrix}\begin{bmatrix}0\\0\\1\\0\end{bmatrix}$$

$$= [0\ 0\ 0\ 1]\begin{bmatrix}0\\0\\0\\-2\lambda E_0\end{bmatrix} = -2\lambda E_0 \Rightarrow E_3^{(2)} = \frac{(-2\lambda E_0)^2}{-4E_0} = -\lambda^2 E_0$$

Similarly, $E_4^{(2)} = \lambda^2 E_0$

Energy correction upto second order

$$E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = E_0 + \lambda E_0 = (1+\lambda)E_0$$

$$E_2 = E_2^{(0)} + E_2^{(1)} + E_2^{(2)} = 8E_0$$

$$E_3 = E_3^{(0)} + E_3^{(1)} + E_3^{(2)} = \left(3-\lambda^2\right)E_0$$

$$E_4 = E_4^{(0)} + E_4^{(1)} + E_4^{(2)} = \left(7+\lambda^2\right)E_0$$

First order correction to wave functions

$$\left|\psi_1^{(1)}\right\rangle = \sum_{m=2,3,4} \frac{<\phi_m|\hat{H}_p|\phi_1>}{E_1^{(0)}-E_m^{(0)}}|\phi_m\rangle = \begin{bmatrix}0\\0\\0\\0\end{bmatrix} \Rightarrow |\psi_1\rangle = |\phi_1\rangle + \left|\psi_1^{(1)}\right\rangle = \begin{bmatrix}1\\0\\0\\0\end{bmatrix}$$

$$\left|\psi_2^{(1)}\right\rangle = \sum_{m=1,3,4} \frac{<\phi_m|\hat{H}_p|\phi_1>}{E_2^{(0)}-E_m^{(0)}}|\phi_m\rangle = \begin{bmatrix}0\\0\\0\\0\end{bmatrix} \Rightarrow |\psi_2\rangle = |\phi_2\rangle + \left|\psi_2^{(1)}\right\rangle = \begin{bmatrix}0\\1\\0\\0\end{bmatrix}$$

$$|\psi_3^{(1)}\rangle = \sum_{m=1,2,4} \frac{\langle \phi_m | \hat{H}_p | \phi_3 \rangle}{E_3^{(0)} - E_m^{(0)}} |\phi_m\rangle = \frac{\langle \phi_1 | \hat{H}_p | \phi_3 \rangle}{E_3^{(0)} - E_1^{(0)}} |\phi_1\rangle + \frac{\langle \phi_2 | \hat{H}_p | \phi_3 \rangle}{E_3^{(0)} - E_2^{(0)}} |\phi_2\rangle + \frac{\langle \phi_4 | \hat{H}_p | \phi_3 \rangle}{E_3^{(0)} - E_4^{(0)}} |\phi_4\rangle$$

$$= \frac{2\lambda E_0}{4E_0} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \frac{\lambda}{2} \end{bmatrix} \quad \Rightarrow |\psi_3\rangle = |\phi_3\rangle + |\psi_3^{(1)}\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 0 \\ \frac{\lambda}{2} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ \frac{\lambda}{2} \end{bmatrix}$$

$$|\psi_4^{(1)}\rangle = \sum_{m=1,2,3} \frac{\langle \phi_m | \hat{H}_p | \phi_4 \rangle}{E_4^{(0)} - E_m^{(0)}} |\phi_m\rangle = \begin{bmatrix} 0 \\ 0 \\ -\frac{\lambda}{2} \\ 0 \end{bmatrix}; \quad \Rightarrow |\psi_4\rangle = |\phi_4\rangle + |\psi_4^1\rangle = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ -\frac{\lambda}{2} \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ -\frac{\lambda}{2} \\ 1 \end{bmatrix}$$

DEGENERATE PERTURBATION THEORY

The degenerate perturbation theory is used to calculate the energy eigenvalues and eigen states of the system when the unperturbed Hamiltonian $\hat{H}_0$ is degenerate.

Let the total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_p$

$$\hat{H} | \psi_n > = \left(\hat{H}_0 + \hat{H}_p\right) | \psi_n > = E_n | \psi_n > \quad \ldots (1)$$

Now suppose that $\hat{H}_0$ has f fold degenerate eigen values $E_n^{(0)}$ i.e. these exist a set of 'f' different eigen states $|\phi_{n\alpha}\rangle$ where $\alpha_i = 1, 2, \ldots\ldots f$, that have same energy

$$\hat{H}_0 |\phi_{n\alpha}\rangle = E_n^{(0)} |\phi_{n\alpha}\rangle \quad \ldots (2)$$

E_n^0 are independent of quantum numbers α suppose we can write the eigenfunction $| \psi_n >$ as a linear combination in terms of $|\phi_{n\alpha}\rangle$

$$|\psi_n\rangle = \sum_{\alpha=1}^{f} a_\alpha |\phi_{n\alpha}\rangle \quad \ldots (3)$$

Consider $\{|\phi_{n\alpha}\rangle\}$ is a arthonormal basis

$$\langle \phi_{n\beta} | \phi_{n\alpha} \rangle = \delta_{\alpha\beta} \quad \ldots (4)$$

And $|\psi_n\rangle$ is normalized.

To determine first order correction to energy substitute equation (3) into (1)

$$\left[\hat{H}_0 + \hat{H}_p\right] \sum_\alpha a_\alpha | \phi_{n\alpha} > = E_n \sum_\alpha a_\alpha | \phi_{n\alpha} >$$

$$\Rightarrow \sum_\alpha \left[E_n^0 + \hat{H}_p\right] a_\alpha |\phi_{n\alpha}\rangle = E_n \sum_\alpha a_\alpha |\phi_{n\alpha}\rangle$$

$$\Rightarrow \sum_\alpha a_\alpha \left[E_n^{(0)} < \phi_{n\beta} | \phi_{n\alpha} > + < \phi_{n\beta} | \hat{H}_p | \phi_{n\alpha} > \right] = E_n \sum_\alpha a_\alpha < \phi_{\alpha\beta} | \phi_{n\alpha} >$$

$$\Rightarrow \sum_\alpha a_\alpha E_n^{(0)} \delta_{\alpha\beta} + \sum_\alpha a_\alpha < \phi_{n\beta} | \hat{H}_p | \phi_{n\alpha} > = \sum_n E_n a_\alpha \delta_{\alpha\beta}$$

$$\Rightarrow -\sum_{\alpha} a_\alpha \left(E_n - E_n^{(0)}\right)\delta_{\alpha\beta} + \sum_{\alpha} a_\alpha \left\langle \phi_{n\beta} \middle| \hat{H}_p \middle| \phi_{n\alpha} \right\rangle = 0 \quad \ldots (5)$$

We can write this equation as

$$\sum_{\alpha}\left[\hat{H}_{p_{\alpha\beta}} - E_n^{(1)}\delta_{\alpha\beta}\right] a_\alpha = 0 \quad \ldots (6)$$

where, $E_n^{(1)} = E_n - E_n^{(0)}$; $\hat{H}_{p_{\alpha\beta}} = \left\langle \phi_{n\beta} \mid \hat{H}_p \mid \phi_{n\alpha} \right\rangle$

$\sum_{\alpha=1}^{f}\left[\hat{H}_{p_{\alpha\beta}} - E_n^{(1)}\,\delta_{\alpha\beta}\right] a_\alpha = 0$ is a set of 'f' homogenous linear equation for a_α.

The coefficients a_α are non-vanishing only when the determinant of coefficient of a_α is zero.

$$\begin{vmatrix} \hat{H}_{p_{11}} & \hat{H}_{p_{12}} & \hat{H}_{p_{13}} & \cdots & \hat{H}_{p_{1f}} \\ \hat{H}_{p_{21}} & \hat{H}_{p_{22}} & \hat{H}_{p_{23}} & \cdots & \hat{H}_{p_{2f}} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \hat{H}_{pf1} & \hat{H}_{pf2} & \hat{H}_{pf3} & \cdots & \hat{H}_{pff} \end{vmatrix} = 0$$

This is a f^{th} degree equation in $E_{n\alpha}^{(1)}$

It has f roots of $E_{n\alpha}^{(1)}$. These roots are first order correction to the eigen values $E_{n\alpha}$ of $\hat{H}$. To calculate $|H_n>$ we need a_α that are calculated by substituting the roots in equation (6). The roots of $E_{n\alpha}^{(1)}$ are in general different. In this case $\hat{H}$ has different eigenvalues (or non degenerate eigenvalue). Hence the f-fold degenerate level E_n^0 of perturbed system in split in f different level $E_{n\alpha}$. In this perturbation lefts the degeneracy or remove the degeneracy. The lifting of degeneracy may be either total or partial, depending an whether all roots or only some of them are different.

Note: Degenerate perturbation theory is in brief to calculate first order energy correction and eigenstates to zero order for an f-fold degenerate level.

1. First determine $\begin{vmatrix} \hat{H}_{p_{11}} & \hat{H}_{p_{12}} & \hat{H}_{p_{13}} & \cdots & \hat{H}_{p_{1f}} \\ \hat{H}_{p_{21}} & \hat{H}_{p_{22}} & \hat{H}_{p_{23}} & \cdots & \hat{H}_{p_{2f}} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \hat{H}_{pf1} & \hat{H}_{pf2} & \hat{H}_{pf3} & \cdots & \hat{H}_{pff} \end{vmatrix}_{f\times f}$ where $\hat{H}_{p_{\alpha\beta}} = < \phi_{n\alpha} \mid \hat{H}_p \mid \phi_{n\beta} >$

2. Diagonalise this matrix and find f eigen values $E_n^1 (\alpha = 1,2,\ldots\ldots)$ and their corresponding eigen states

$$|\phi_{n\alpha\beta}\rangle = \begin{pmatrix} a_{\alpha 1} \\ a_{\alpha 2} \\ .. \\ .. \\ a_{\alpha f} \end{pmatrix}$$

The energy eigen values corrected upto first order $E_{n\alpha} = E_n^{(0)} + E_{n\alpha}^{(1)}$

and corresponding eigenvectors $|\psi_{n\alpha}\rangle = \sum_{\beta=1}^{f} a_{\alpha\beta}|\phi_{n\beta}\rangle$

Stark Effect in Hydrogen atom: The spliting of energy level of an atom caused by uniform external electric field E is called stark-effect.

Problem: Using the first order (degenerate) perturbation theory, calculate the energy levels of the n= 1, n = 2 states of a hydrogen atom placed in an external uniform weak electric field along the +ve z-axis.

Soln: The force on the electron in an electric field is $F = -eE$.

Then potential energy due to this force $= -eEz$

The Hamiltonian for hydrogen atom

$$\hat{H} = \hat{H}_0 + \hat{H}_p = \left(\frac{-\hbar^2\nabla^2}{2m} - \frac{Ze^2}{r} - eEz\right) \Rightarrow \hat{H}_0 = -\frac{\hbar^2\nabla^2}{2m} - \frac{Ze^2}{r}$$

$$\hat{H}_p = -eEz; \quad \hat{H}_p = -eEr\cos\theta$$

Potential energy is spherically symmetric

First order stark effect for (n = 1) ground state for hydrogen atom

$n = 1,\ \ell = 0, m = 0$

$\psi_{n\ell m} = \psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$; Ground state is non-degenerate.

Then the first order energy correction in ground state.

$$E_1^{(1)} = \langle\psi_{100}|\hat{H}_p|\psi_{100}\rangle$$

$$= -eE\langle\psi_{100}|\hat{H}_p|\psi_{100}\rangle = -eE\langle\psi_{100}|r\cos\theta|\psi_{100}\rangle$$

$$= \frac{-eE}{\pi E_0^3}\int_0^{\infty} e^{-\frac{2r}{a_0}} r^3 dr \int_0^{\pi} \sin\theta\cos\theta d\theta \int_0^{2\pi} d\phi = 0$$

For ground state of hydrogen atom there is no first order stark effect.

First order stark effect in first excited state (n = 2) for H-atom

For n = 2; $\ell = 0,1$; m = 0, 1, 0, –1

The state $|n,\ell,m\rangle$; $|1200\rangle, |1210\rangle, |1211\rangle, |121\bar{1}\rangle$ are four possible combinations.

Since energy depends only on 'n' so the first excited state are four fold degenerate in the absence of perturbation.

determinant

$$\hat{H}_p = \begin{vmatrix} \langle 200|\hat{H}_p|200\rangle & \langle 200|\hat{H}_p|210\rangle & \langle 200|\hat{H}_p|211\rangle & \langle 200|\hat{H}_p|21\bar{1}\rangle \\ \langle 210|\hat{H}_p|200\rangle & \langle 210|\hat{H}_p|210\rangle & \langle 210|\hat{H}_p|211\rangle & \langle 210|\hat{H}_p|21\bar{1}\rangle \\ \langle 211|\hat{H}_p|200\rangle & \langle 211|\hat{H}_p|210\rangle & \langle 21\bar{1}|\hat{H}_p|\bar{2}11\rangle & \langle 211|\hat{H}_p|21\bar{1}\rangle \\ \langle 21\bar{1}|\hat{H}_p|200\rangle & \langle 21\bar{1}|\hat{H}_p|210\rangle & \langle 21\bar{1}|\hat{H}_p|211\rangle & \langle 21\bar{1}|\hat{H}_p|21\bar{1}\rangle \end{vmatrix}$$

The matrix element can be calculated more simply by using the relevant selection rules and symmetries

1. Since $\langle n\ell' m'|\hat{H}_p|n\ell m\rangle$ do not depend on ϕ so, it is non zero only if $m' = m-$

2. As $z = r\cos\theta$ is odd, so, for $\langle n\ell' m'|\hat{H}_p|n\ell m\rangle$ must be non zero $|n\ell' m'\rangle$ and $|n\ell m\rangle$ must be opposite parities it means only for these matrix elements are non zero that couple with 2s and 2p.

$$\hat{H}_p = \begin{vmatrix} 0 & \langle 200|\hat{H}_p|210\rangle & 0 & 0 \\ \langle 210|\hat{H}_p|200\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} \quad \ldots (1)$$

Then diagonalize the matrix of $\hat{H}_p$ or secular determinant.

$$\begin{vmatrix} -E_2^{(1)} & \langle 200|\hat{H}_p|210\rangle & 0 & 0 \\ \langle 210|\hat{H}_p|200\rangle & E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0 \quad \ldots (2)$$

$$\langle 200|\hat{H}_p|210\rangle = \left(\langle 210|\hat{H}_p|200\rangle\right)^*$$

$$\psi_{200} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$$

$$\psi_{210} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(\frac{r}{a_0}\cos\theta\right)e^{-\frac{r}{2a_0}}$$

$$\langle 200|\hat{H}_p|210\rangle = -eE\int_0^\infty\int_0^\pi\int_0^{2\pi}\frac{1}{32\pi a_0^3}\left(2-\frac{r}{a_0}\right)e^{\frac{r}{2a_0}}r\cos\theta\left(\frac{r}{a_0}\right)\cos\theta\, e^{\frac{r}{a_0}}\, r^2 dr\sin\theta d\theta d\phi$$

$$= -\frac{eE}{32\pi a_0^4}\int_0^\infty e^{\frac{r}{a_0}}\left(2-\frac{r}{a_0}\right)r^4 dr\int_0^\pi\cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi$$

$$\int_0^{\pi}\cos^2\theta\sin\theta d\theta=\frac{2}{3};\quad \int_0^{\infty}r^5e^{-\frac{r}{a_0}}dr=\frac{5!}{\left(\frac{1}{a_0}\right)^6};\quad \int_0^{\infty}r^4e^{-\frac{r}{a_0}}dr=\frac{4!}{\left(\frac{1}{a_0}\right)^5}$$

$$<200|\hat{H}_p|210>=\left(\frac{-eE\times2\pi}{32\pi a_0^4}\right)\left[2\times41a_0^5-\frac{1}{a_0}5!a_0^6\right]\times\frac{2}{3}=\left(\frac{-eE}{16a_0^4}\right)\times a_0^5[48-120]\times\frac{2}{3}$$

$$=\frac{-eEa_0}{8\times3}\times72=3eEa_0=\langle210|\hat{H}_p|200\rangle$$

Substituting these values in equation (2)

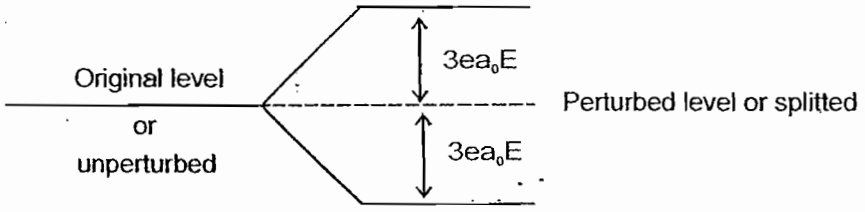
$$\begin{vmatrix}-E_2^{(1)} & 3eEa_0 & 0 & 0\\ 3eEa_0 & -E_2^{(1)} & 0 & 0\\ 0 & 0 & -E_2^{(1)} & 0\\ 0 & 0 & 0 & -E_2^{(1)}\end{vmatrix}=0$$

$$\left(E_2^{(1)}\right)^2\left[\left(E_2^{(1)}\right)^2-(3eEa_0)^2\right]=0$$

$$E_2^{(1)}=0,0\Rightarrow E_2^{(1)}=0,\ E_2^{(1)}=0$$

$$E_2^{(1)}=\pm3eE_{a0}\Rightarrow E_2^{(1)}=3ea_0E,\ E_2^{(1)}=-3ea_0E$$

Out of four fold degeneracy, two fold degeneracy is removed.



The electric potential energy of a dipole is $E=-\bar{P}.\bar{E}$
Hence, the behaviour of hydrogen atom in (n = 2) first excited state is like a permanent dipole moment of magnitude is zero. Which can be oriented in three different ways.
(1) One state parallel to external electric field E
(2) One state anti parallel to external electric field E
(3) Two state perpendicular to external electric field E

Now suppose $\psi=\begin{bmatrix}\alpha_1\psi_{200}\\ \alpha_2\psi_{210}\\ \alpha_3\psi_{211}\\ \alpha_4\psi_{211}\end{bmatrix}\Rightarrow|\psi\rangle=\Sigma\alpha_i|n\ell m>$

(i) Eigenfunction for $E_2^{(1)}=0$

$$\begin{bmatrix} 0 & 3ea_0e & 0 & 0 \\ 3ea_0E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} \alpha_1\psi_{200} \\ \alpha_2\psi_{210} \\ \alpha_3\psi_{211} \\ \alpha_4\psi_{211} \end{bmatrix} = 0 \quad ; \quad \begin{aligned} 3ea_0E\ \alpha_2\psi_{210} = 0 &\Rightarrow \alpha_2 = 0 \\ 3ea_0E\ \alpha_1\psi_{200} = 0 &\Rightarrow \alpha_1 = 0 \end{aligned}$$

Then ψ is given by $\psi = \alpha_3\ \psi_{21\bar{1}} + \alpha_4\psi_{21\bar{1}}$

Using normalization and $|\alpha_3|^2 + |\alpha_4|^2 = 1$

$$\alpha_3 = \frac{1}{\sqrt{2}}, \alpha_4 = \frac{1}{\sqrt{2}} \qquad \Rightarrow \alpha_3 = \frac{1}{\sqrt{2}}, \alpha_4 = -\frac{1}{\sqrt{2}}$$

The correct linear combination is $\frac{1}{\sqrt{2}}\left[\psi_{21\bar{1}} + \psi_{2\pi}\right]$ & $\frac{1}{\sqrt{2}}\left[\psi_{21\bar{1}} - \psi_{21\bar{1}}\right]$

(ii) Eigenfunction for $E_2^{(1)} = 3eEa_0$

$$\begin{bmatrix} -3ea_0E & 3ea_0e & 0 & 0 \\ 3ea_0E & -3ea_0E & 0 & 0 \\ 0 & 0 & -3ea_0E & 0 \\ 0 & 0 & 0 & -3ea_0E \end{bmatrix}\begin{bmatrix} \alpha_1\psi_{200} \\ \alpha_2\psi_{210} \\ \alpha_3\psi_{211} \\ \alpha_4\psi_{21\bar{1}} \end{bmatrix} = 0$$

$$-3eEa_0\alpha_1\psi_{200} + 3ea_0E\alpha_2\psi_{210} = 0$$

$$\alpha_1\psi_{200} - \alpha_2\psi_{210} = 0$$

$$-3ea_0E\alpha_3\psi_{211} = 0 \Rightarrow \alpha_3 = 0 \quad \Rightarrow \alpha_4 = 0 \quad \Rightarrow |\alpha_1|^2 + |\alpha_2|^2 = 1$$

$$\psi = \alpha_1\psi_{200} - \alpha_1\psi_{210} = \frac{1}{\sqrt{2}}\left[\psi_{200} - \psi_{210}\right]$$

(iii) Eigenfunction for $E_2^{(1)} = -3eEa_0$; $\psi = \frac{1}{\sqrt{2}}[\psi_{200} + \psi_{210}]$

Problem. A system, with an unperturbed Hamiltonian

$$\hat{H}_0 = E_0\begin{pmatrix} 15 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}, \quad \hat{H}_p = \frac{E_0}{100}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

(a) Find the exact eigenvalues and exact eigenfunctions of unperturbed Hamiltonian $\hat{H}_0$.

(b) Find the eigen energies to first-order correction.

Soln. **(a)** Eigen energies of unperturbed Hamiltonian $\hat{H}_0$ are $E_1^{(0)} = 15$, $E_2^{(0)} = E_3^{(0)} = E_4^{(0)} = 3$

Three fold degenerate and eigenstates

$$|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad |\phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 1 \end{pmatrix}$$

Suppose $\lambda = \frac{1}{100}$; $\hat{H} = \begin{bmatrix} 15E_0 & 0 & 0 & 0 \\ 0 & 3E_0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 3E_0 & 0 \\ 0 & 0 & 0 & 3E_0 \end{bmatrix}$

The diagonalization of this gives the exact eigenvalue of $\hat{H}$

$$\begin{bmatrix} 15E_0 - E^{(1)} & 0 & 0 & 0 \\ 0 & 3E_0 - E^{(1)} & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 3E_0 - E^{(1)} & 0 \\ 0 & 0 & 0 & 3E_0 - E^{(1)} \end{bmatrix} = 0$$

$$\left(3E_0 - E^{(1)}\right)\left(15E_0 - E^{(1)}\right)\left[(3E_0 - E)^2 - \lambda E_0^2\right]$$

$$= E_1^{(1)} = 3E_0\,; \quad E_2^{(1)} = 15E_0; \quad E_3^{(1)} = (3-\lambda)E_0; \quad E_4^{(1)} = (3+\lambda)L$$

(b) Using perturbation theory

$$E_1^{(1)} = \langle \phi_1 | H_p | \phi_1 \rangle = \begin{bmatrix} 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = 0$$

E_1 correction upto first order

$E_1 = E_1^{(0)} + E_1^{(1)} = 15E_0$

$E_2^0 = E_3^0 = E_4^0$ are three fold degenerate to find first order correction we find secular determinant.

$$\begin{bmatrix} H_{22} - E^{(1)} & H_{23} & H_{24} \\ H_{32} & H_{33} - E^{(1)} & H_{34} \\ H_{42} & H_{43} & H_{44} - E^{(1)} \end{bmatrix}_{3\times 3} = 0$$

$$H_{22} = \langle \phi_2 | \hat{H}_p | \phi_2 \rangle = \begin{bmatrix} 0 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} = 0$$

$$H_{23} = \langle \phi_2 | \hat{H}_p | \phi_3 \rangle = \begin{bmatrix} 0 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} = \lambda E_0$$

$$H_{32} = \langle \phi_3 | \hat{H}_p | \phi_2 \rangle = \langle \phi_2 | \hat{H}_p | \phi_3 \rangle^* = \lambda E_0$$

$$H_{24} = \langle \phi_2 | \hat{H}_p | \phi_4 \rangle = 0$$

$$H_{42} = \langle \phi_2 | \hat{H}_p | \phi_4 \rangle^* = 0$$

$$H_{43} = \langle \phi_4 | \hat{H}_p | \phi_4 \rangle = 0$$

$$H_{34} = \langle \phi_3 | \hat{H}_p | \phi_4 \rangle = 0$$

$$H_{44} = \langle \phi_4 | \hat{H}_p | \phi_4 \rangle = 0$$

Secular determinant

$$\begin{bmatrix} -E^{(1)} & \lambda E_0 & 0 \\ \lambda E_0 & -E^{(1)} & 0 \\ 0 & 0 & -E^{(1)} \end{bmatrix} = 0$$

$$E^{(1)}\left[\left(E^{(1)}\right)^2 - \lambda^2 E_0^2\right] = 0;\ E_2^{(1)} = 0;\quad E_3^{(1)} = -\lambda E_0;\ E_4^{(1)} = \lambda E_0$$

Energy correction upto first order

$$E_1 = E_1^{(1)} + E_1^{(0)} = 15E_0, \qquad E_3 = E_3^{(0)} + E_3^{(1)} = 3E_0 - \lambda E_0$$

$$E_2 = E_2^{(1)} + E_2^{(1)} = 3E_0, \qquad E_0 = E_4^{(0)} + E_4^{(1)} = 3E_0 + \lambda E_0$$

Problem. Consider the three dimensional infinite potential cubic well

$$V(x,y,z) = \begin{cases} 0 & \text{if } 0 < x < a,\ 0 < y < a \ \&\ 0 < z < a \\ \alpha & \text{otherwise} \end{cases}$$

The unperturbed state are

$$\psi_{x,y,z}^{(0)} = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{a}\right)\sin\left(\frac{n_z \pi z}{a}\right) \text{ and eigenvalues are}$$

$$E_{n_x,n_y,n_z}^{(0)} = \frac{\hbar^2\pi^2}{2ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]$$

Let us introduce the perturbation $\hat{H}_p = \lambda H'$

$$H' = \begin{cases} V_0 & \text{if } 0 < x < a/2,\ 0 < y < a/2 \\ 0 & \text{otherwise} \end{cases}$$

Find the energy correction upto first order for ground and first excited state.

Soln. The ground state ψ_{111} is non degenerate

$$E_0^{(0)} = \frac{3\pi^2\hbar^2}{2ma^2}$$

First order correction to E_0

$$E_0^{(1)} = \left\langle \psi_{111} \middle| \hat{H}' \middle| \psi_{111} \right\rangle$$

$$= \left(\frac{2}{a}\right)^3 \left[\int_0^{a/2}\int_0^{a/2}\int_0^{a} \sin\frac{\pi x}{a} H' \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{\pi z}{a}\right)\sin\left(\frac{\pi z}{a}\right) dx\, dy\, dz\right]$$

$$=\left(\frac{2}{a}\right)^3\left[V_0\int_0^{a/2}\sin^2\frac{\pi x}{a}dx\int_0^{a/2}\sin^2\frac{\pi y}{a}dy\int_0^{a}\sin^2\frac{\pi z}{a}dz\right]=\left(\frac{2}{a}\right)^3 V_0\left[\left(\frac{1}{2}.\frac{a}{2}\right).\left(\frac{1}{2}.\frac{a}{2}\right).\left(\frac{1}{2}.a\right)\right]=\frac{V_0}{4}$$

Ground state energy correct upto first order, $E_0=E_0^{(0)}+E_0^{(1)}=\frac{3\pi^2\hbar^2}{2ma^2}+\frac{V_0}{4}$

The first excited state ψ_{112} is degenerate with energy $E_1=\frac{6}{2}\frac{\hbar^2\pi^2}{ma^2}$

$\psi_a=\psi_{112};\quad \psi_b=\psi_{121};\quad \psi_c=\psi_{211}$

Perturbed Hamiltonian correction matrix

$$\begin{bmatrix} H'_{aa} & H'_{ab} & H'_{ac} \\ H'_{ba} & H'_{bb} & H'_{bc} \\ H'_{ca} & H'_{cb} & H'_{cc} \end{bmatrix}$$

$$H'_{aa}=H'_{bb}=H'_{cc}=\frac{1}{4}V_0$$

$$H'_{ab}=H'_{ba}=\langle\psi_{112}|H'|\psi_{121}\rangle=\left(\frac{2}{a}\right)^3 V_0\int_0^{a/2}\sin^2\frac{\pi x}{a}dx\int_0^{a/2}\sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{2\pi y}{a}\right)dy\int_0^{a}\sin\left(\frac{2\pi z}{a}\right)\sin\left(\frac{\pi z}{a}\right)=0$$

$$H'_{ac}=0=H'_{ca}$$

$$H'_{bc}=\left(\frac{2}{a}\right)^3 V_0\int_0^{a/2}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx\int_0^{a/2}\sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{2\pi y}{a}\right)dy\int_0^{a}\sin^2\left(\frac{\pi z}{a}\right)dz=\frac{16}{9\pi^2}V_0$$

$$H'=\frac{V_0}{4}\begin{bmatrix}1&0&0\\0&1&\frac{64}{9\pi^2}\\0&\frac{64}{9\pi^2}&1\end{bmatrix};\quad \text{Secular determinant,}\begin{vmatrix}\frac{V_0}{4}-E_1^{(1)}&0&0\\0&\frac{V_0}{4}-E_1^{(1)}&\frac{16V_0}{9\pi^2}\\0&\frac{16V_0}{9\pi^2}&\frac{V_0}{4}-E_1^{(1)}\end{vmatrix}=0$$

$$\Rightarrow\quad \left(\frac{V_0}{4}-E_1^{(1)}\right)\left[\left(\frac{V_0}{4}-E_1\right)^2-\left(\frac{16V_0}{9\pi^2}\right)\right]=0$$

$$\Rightarrow\quad E_1^{(1)}=\frac{V_0}{4},\ \frac{V_0}{4}+\frac{16V_0}{9\pi^2},\ \frac{V_0}{4}-\frac{16V_0}{9\pi^2}$$

First excited state energy correction upto first order

$$E_1=\begin{cases}E_1^{(0)}+\lambda\frac{V_0}{4}\\ E_1^{(0)}+\lambda\left(\frac{V_0}{4}+\frac{16}{9\pi^2}V_0\right]\\ E_1^{(0)}+\lambda\left(\frac{V_0}{4}-\frac{16}{9\pi^2}V_0\right];\end{cases}\quad \psi^0=\begin{cases}\psi_a\\ (\psi_b+\psi_c)\sqrt{2}\\ (\psi_b+\psi_c)/\sqrt{2}\end{cases}$$

TIME DEPENDENT PERTURBATION THEORY

When the Hamiltonian of a system depends on the time, there are no stationary state solutions of Schrodinger equation. It is generally impossible to obtain exact solutions of the Schrodinger equation when Hamiltonian depends upon time. Therefore such an equation is solved by time-dependent perturbatian theory. Time dependent perturbation thoery is most useful for studying process of absorption and emission of radiation by atoms or more generally, for treating the transitions of the quantum mechanical systems from one energy level to another.

The total Hamiltonian of the system is given by

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \qquad ...(1)$$

Where H_0 = time independent Hamiltonian which describes the system when unperturbed is assumed to have exact solution that are known with eigenvalues E_n and eigenstates $|\psi_n\rangle$

$$H_0|\psi_n\rangle = E_n|\psi_n\rangle \qquad ...(2)$$

In the interval $0 \le t \le \tau$ we subject the system to an external time-dependent perturbation which is small compared to $\hat{H}_0$

$$\hat{V}(t) = \begin{cases} \hat{V}(t) & 0 \le t \le \tau \\ 0 & t < 0,\ t > \tau \end{cases} \qquad ... (3)$$

The Schrodinger equation for the time dependent Hamiltonian $\hat{H}$

$$\hat{H}|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle \qquad ...(4)$$

The main task of time dependent perturbation theory consist of answering the question how system undergo transitions from one unperturbed state to another or what is the probability that the system will be found at a later time in another unperturbed eigen state $|\psi_f\rangle$?

Transition Probability:

The transition probability from an initial unperturbed state $|\psi_i\rangle$ to another perturbed state $|\psi_f\rangle$ is given by

$$P_{if}(t) = \left|-\frac{i}{\hbar}\int_0^t \langle\psi_f|\hat{V}(t')|\psi_i\rangle e^{i\omega_{fi}t'}dt'\right|^2 \qquad ... (5)$$

Where $\omega_{fi} = \dfrac{(E_f - E_i)}{\hbar}$

Transition Probability for a constant Perturbation $\hat{V}(t) = \text{constant}$

$$P_{if}(t) = \frac{1}{\hbar^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\int_0^t e^{i\omega_{fi}t'}dt'\right|^2 = \frac{1}{\hbar^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2\left|\frac{e^{i\omega_{fi}t'}}{\omega_{fi}}\right|_0^t\Bigg|^2 = \frac{1}{\hbar^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2\left|\frac{e^{i\omega_{fi}t}-1}{\omega_{fi}}\right|^2$$

$$= \frac{1}{h^2\omega_{fi}^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2\left(e^{-i\omega_{fi}t}-1\right)\left(e^{i\omega_{fi}t}-1\right) = \frac{1}{h^2\omega_{fi}^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2\left[1+1-\left(e^{i\omega_{fi}t}+e^{-i\omega_{fi}t}\right)\right]$$

$$= \frac{1}{h^2\omega_{fi}^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 (2-2\cos\omega_{fi}t) = \frac{1}{h^2\omega_{fi}^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 2\left(1+2\sin^2\frac{\omega_{fi}}{2}-1\right)$$

$$P_{if}(t) = \frac{4}{h^2\omega_{fi}^2}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 \sin^2\left(\frac{\omega_{fi}t}{2}\right) \qquad ...(6)$$

The transition probability is an oscillating sinusoidal function with a period of $\frac{2\pi}{\omega_{fi}}$

P_{if} is maximum at t = 0 as $\lim_{\omega_{fi}\to 0} \frac{\sin^2\left(\frac{\omega_{fi}t}{2}\right)}{\frac{\omega_{fi}^2t^2}{4}} = 1 \quad \Rightarrow \quad \lim_{\omega_{fi}\to 0} \frac{\sin^2\left(\frac{\omega_{fi}t}{2}\right)}{\omega_{fi}^2} = \frac{t^2}{4}$

Height of the curve of equation (6) is $\propto t^2$ and width $\propto \frac{1}{t}$, so area proportional to t.

$$\lim_{g\to\infty} \frac{\sin^2 gx}{\pi x^2 g} = \delta(x) \qquad ... (7)$$

$$\lim_{t\to\infty} \frac{\sin^2\left(\frac{\omega_{fi}t}{2}\right)}{\left(\frac{\omega_{fi}^2t}{4}\right)} = \pi t\delta\left(\frac{\omega_{fi}}{2}\right) = 2\pi\delta(\omega_{fi}) \qquad ... (8)$$

From equation (6) & (8), $P_{if}(t) = \frac{2\pi t}{h^2}|V_{fi}|^2\,\delta(\omega_{fi})$ ... (9)

$$\delta(\omega_{fi}) = h\delta(E_f - E_i) = \frac{2\pi}{h}t|V_{fi}|^2\,\delta(E_f - E_i) \qquad ... (10)$$

The transition rate (transition probability per unit time)

$$W_{if} = \frac{dP_{if}}{dt}(t) = \frac{2\pi}{h}|V_{fi}|^2\,\delta(E_f - E_i) \qquad ... (11)$$

The factor $\delta(E_f - E_i)$ guaranteed the conservation of energy. In the limit $t \to \infty$ the transition rate is nonvanishing only between states of equal energy. Hence a constant time independent perturbation neither removes energy from the system nor supplies energy to it. It simply causes energy conserving transitions.

Transition into a continuum of final states: Let us now calculate total transition rate associated with a transition from initial state $|\psi_i>$ in to a continuum of final states $|\psi_f>$ If $\rho(E_f)$ is the density of final states.

Number of states per unit energy interval.

The number of final states within the energy interval E_f & $E_f + dE_f$ is equal to $\rho(E_f)\,dE_f$

The total transition rate

$$W_{if} = \int \frac{dP_{if}}{dt}\rho(E_f)\,dE_f = \frac{2\pi}{h}\left|\psi_f|\hat{V}|\psi_i>\right|^2 \int\rho(E_f)\delta(E_f - E_i)\,dE_f$$

$$W_{if} = \frac{2\pi}{h}\left|<\psi_f|\hat{V}|\psi_i>\right|^2 \rho(E_f) \qquad ... (12)$$

This is called fermi golden rule

(i) W_{fi} is non zero between two continuum states of same energy

(ii) Proportional to $|H_{fi}|^2$

(iii) Proportional to density of final states

Problem 1: A particle, which is initially ($t = 0$) in the ground state of an infinite, one-dimensional potential box with walls at $x = 0$ and $x = a$, is subjected for $0 \le t \le \infty$ to a perturbation $\hat{V}(t) = \hat{x}^2 e^{-1/\tau}$. Calculate to first order the probability of finding the particle in its first excited state for $t \ge 0$.

Soln. For a particle in a box potential, with $E_n = n^2\pi^2\hbar^2/(2ma^2)$ and $\psi_n = \sqrt{2/a}\sin(n\pi x/a)$, the ground state corresponds to $n = 1$ and the first excited state to $n = 2$.

$$P_{12} = \frac{1}{\hbar^2}\left|\int_0^\infty \left\langle \psi_2 \middle| \hat{V}(t) \middle| \psi_1 \right\rangle e^{i\omega_{21}t}\right|^2 = \frac{1}{\hbar^2}\left|\left\langle \psi_2 \middle| \hat{x}^2 \middle| \psi_1 \right\rangle\right|^2 \left|\int_0^\infty e^{-(1/\tau - i\omega_{21})t}dt\right|^2 \quad ...(1)$$

where, $$\left\langle \psi_2 \middle| \hat{x}^2 \middle| \psi_1 \right\rangle = \int_0^a x^2 \psi_2^*(x)\psi_1(x)dx = \frac{2}{a}\int_0^a x^2 \sin\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)dx = -\frac{16a^2}{9\pi^2} \quad ... (2)$$

$$\left|\int_0^t e^{-(1/\tau - i\omega_{21})t}dt\right|^2 = \left|\frac{e^{-(1/\tau - i\omega_{21})t} - 1}{\frac{1}{\tau} - i\omega_{21}}\right|^2 = \frac{1 + e^{-2t/\tau} - 2e^{-t/\tau}\cos(\omega_{21}t)}{\omega_{21}^2 + 1/\tau^2} \quad ...(3)$$

which, in the limit $t \to \infty$, reduces to

$$\left|\int_0^\infty e^{-(1/\tau - i\omega_{21})t}dt\right|^2 = \left[\omega_{21}^2 + \frac{1}{\tau^2}\right]^{-1} = \left[\frac{9\pi^4\hbar^2}{4m^2a^4} + \frac{1}{\tau^2}\right]^{-1} \quad ... (4)$$

since, $\omega_{21} = (E_2 - E_1)/\hbar = 3\pi^2\hbar/(2ma^2)$. A substitution of (2) and (4) into (1) leads to

$$P_{12} = \left(\frac{16a^2}{9\pi^2\hbar}\right)^2 \left[\frac{9\pi^4\hbar^2}{4m^2a^4} + \frac{1}{\tau^2}\right]^{-1} \quad ... (5)$$

Problem 2: A particle is initially ($t < 0$) in the ground state of an infinite, one-dimensional potential well with walls at $x = 0$ and $x = a$.

(a) If the wall at $x = a$ is moved slowly to $x = 8a$, find the energy and wave function of the particle in the new well. Calculate the work done in this process.

(b) If the wall at $x = a$ is now suddenly moved (at $t = 0$) to $x = 8a$, calculate the probability of finding the particle in (i) the ground state, (ii) the first excited state, and (iii) the second excited state of the new potential well.

Soln. For $t < 0$ the particle was in a potential well with walls at $x = 0$ and $x = a$, and hence

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad \psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \qquad (0 \le x \le a)$$

(a) When the wall is moved slowly, the adiabatic theorem dictates that the particle will make no transitions; it will be found at time 't' in the ground state of the new potential well (the well with walls at $x = 0$ and $x = 8a$). Thus, we have

$$E_1(t) = \frac{\pi^2\hbar^2}{2m(8a)^2} = \frac{\pi^2\hbar^2}{128ma^2}, \quad \psi'_1(x) = \sqrt{\frac{2}{8a}}\sin\left(\frac{\pi x}{8a}\right) \quad (0 \le x \le a)$$

The work needed to move the wall is,

$$\Delta W = E_1(t) - E_1 = \frac{\pi^2\hbar^2}{2m(8a)^2} - \frac{\pi^2\hbar^2}{2ma^2} = -\frac{63\pi^2\hbar^2}{128ma^2}$$

(b) When the wall is moved rapidly, the particle will find itself instantly $(\text{at } t \geq 0)$ in the new potential well; its energy levels and wave function are now given by

$$E'_n = \frac{n^2\pi^2\hbar^2}{2m(8a)^2} = \frac{n^2\pi^2\hbar^2}{128ma^2};\ \psi'_n = \sqrt{\frac{2}{8a}}\sin\left(\frac{n\pi x}{8a}\right) \quad (0 \leq x \leq 8a)$$

The probability of findign the particle in the ground state of the new box potential can be obtained from ( ): $P_{11} = |\langle \psi'_1 | \psi_1 \rangle|^2$, where

$$\langle \psi'_1 | \psi_1 \rangle = \int_0^a \psi'^*_1(x)\psi_1(x)\,dx = \frac{2}{\sqrt{8a}}\int_0^a \sin\left(\frac{\pi x}{8a}\right)\sin\left(\frac{\pi x}{a}\right)dx = \frac{16}{63\pi}\sqrt{4-2\sqrt{2}}$$

hence,

$$P_{11} = |\langle \psi'_1 | \psi_1 \rangle|^2 = \left(\frac{16}{63\pi}\right)^2\left(4-2\sqrt{2}\right) = 0.0077 \simeq 0.7\%$$

The probability of finding the particle in the first excited state of new box potential is given by $P_{12} = |\langle \psi'_2 | \psi_1 \rangle|^2$, where,

$$\langle \psi'_2 | \psi_1 \rangle = \int_0^a \psi'^*_2(x)\psi_1(x)\,dx = \frac{2}{\sqrt{8a}}\int_0^a \sin\left(\frac{\pi x}{4a}\right)\sin\left(\frac{\pi x}{a}\right)dx = \frac{8}{15\pi}$$

hence, $P_{12} = |\langle \psi'_2 | \psi_1 \rangle|^2 = \left(\frac{8}{15\pi}\right)^2 = 0.1699 \simeq 17\%$

A similar calculation leads to

$$P_{13} = |\langle \psi'_3 | \psi_1 \rangle|^2 = \left|\frac{2}{\sqrt{8a}}\int_0^a \sin\left(\frac{3\pi x}{8a}\right)\sin\left(\frac{\pi x}{a}\right)dx\right|^2 = \left|\frac{16}{55\pi}\sqrt{4+2\sqrt{2}}\right|^2 \simeq 24.2\%$$

These calculations show that the particle is most likely to be found in higher excited states; the probability of finding it in the ground state is very small..

VARIATIONAL METHOD

There are many problems in Quantum Mechanics they can't be solved exactly or approximately as first order correction is very much different from exact value so it is not sufficiently accurate and 2nd order correction is difficult to evaluate. So, we can't get exact values. So we use variation method.

There are many problems in Quantum Mechanics in which Hamiltonian is knonw but they can't be solved exaclty or approximately by perturbation theory because the first order correction is not sufficiently accurate and it is difficult to calculate higher order correction. One of the approximation methods which is suitable for solving such problems is variational method. It is also known as Rayleigh Ritz method. The variation method is useful for determining upper bound values for the eigen energies of a system whose Hamiltonian is known whereas its eigen values and eigen state are unknown.

In this case $|\psi\rangle$ is variational state. So, expectation value will be $\langle E\rangle = \dfrac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$

$|\psi\rangle$ is variable in this case then $\langle E\rangle = \dfrac{\int\psi^* H\psi d\tau}{\int\psi^*\psi d\tau}$ This is known as variational integral.

Variational method gives upper bound value

If $|\psi\rangle \rightarrow$ trial wave function

If $|\psi\rangle = |\psi_0\rangle$ then eigen value will be E_0.

$\therefore$ eigen value $E \geq E_0$

Proof: The wave function can be expanded in terms of complete set of orthonormal functions or orthonormal basis vectors.

$$|\psi\rangle = \sum_n a_n |\phi_n\rangle$$

$$|\phi_n\rangle = |\phi_1\rangle, |\phi_2\rangle \ldots\ldots |\phi_n\rangle$$

$$\langle\phi_m | \phi_n\rangle = \delta_{nm}$$

Orthonormality condition, $|\psi\rangle = \sum_n a_n |\phi_n\rangle$

Taking Hermitian conjugate, $\langle\psi| = \sum_m a_m^* \langle\phi_m|$

Here we don't take $\sum_n a_n \langle\psi|$ because it we take $a_n \langle\phi_n|$ then we don't get cross terms.

$$|\phi\rangle = C_1|\phi_1\rangle + C_2|\phi_2\rangle$$

$$\langle\phi| = C_1^* \langle\phi_1| + C_2^* \langle\phi_2|$$

$$\langle\psi|\hat{H}|\psi\rangle = \sum_m a_m^* \left\langle\phi_m|\hat{H}|\sum_n a_n|\phi_n\right\rangle = \sum_m\sum_n a_m^* a_n \langle\phi_m|\hat{H}|\phi_n\rangle$$

$$= \sum_m\sum_n a_m^* a_n E_n \langle\phi_m|\phi_n\rangle = \sum_m\sum_n a_m^* a_n E_n \delta_{mn}$$

$$\langle E\rangle = \langle H\rangle = \sum_n |a_n|^2 E_n$$

Here we have openend $\sum_m$ and value will be non zero only for one value when $m = n$.

If E_0 is exact eigen value then difference of two

$$\langle E\rangle - E_0 = \sum_n |a_n|^2 E_n - E_0$$

$$\langle E\rangle - E_0 \geq 0 \qquad \because \text{ Square is always } \geq 0.$$

So, $\langle E\rangle \geq E_0$

So, if we calculate energy eigen value using variational method then eigen value will be always greater than or equal to the exact energy for that particular state. So, it gives upper bound values.

e.g. In case of Harmonic oscillator.

$$V = \frac{1}{2} m\omega^2 x^2 \text{ which is symmetric.}$$

So, wave function must be symmetric i.e. of definite symmetry. e.g. $e^{-\alpha x}$ cannot taken by it does not have exact symmetry. But it can be assumed as trial wave function for particle in box, and $\frac{1}{x^2}$ is also assume as a trial function because at $x = \infty$, it is finite and symmetric. In H_0 we can choose trial function $e^{-\alpha x^2}$ and it depend upon questions form.

Problem: Consider a particle of mass m moving in the potential

$$V(x) = \begin{cases} \infty & x \leq 0 \\ \frac{1}{2} m\omega^2 x^2 & x > 0 \end{cases}$$

Calculate the ground state energy of the particle using variation method.

Soln. Here wave function should be zero for $x = \infty$ as well as when $x \leq 0$ i.e at boundary $x = 0$ wave function must be zero.

$\therefore$ Wave function will be

$$\psi(x) = x e^{-\alpha x^2}$$

It is antisymmetric but still it has definite symmetry. So, it match the eigen function.

$$\langle \hat{H}\rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{H} \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} = \frac{\int_0^{\infty} x e^{-\alpha x^2} \left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\left(x e^{-\alpha x^2}\right) dx + \int_0^{\infty} \frac{1}{2} m\omega^2 x^2 \, x^2 e^{-2\alpha x^2} dx}{\int_0^{\infty} x^2 e^{-\alpha x^2 \cdot 2} dx}$$

$$= \frac{-\frac{\hbar^2}{2m}\int_0^{\infty} x e^{-\alpha x^2} \frac{\partial}{\partial x}\left(x(-2\alpha x) e^{-\alpha x^2} + e^{-\alpha x^2}\right) dx + \frac{1}{2} m\omega^2 \int_0^{\infty} x^4 e^{-2\alpha x^2} dx}{\int_0^{\infty} x^2 e^{-2\alpha x^2} dx}$$

$$= \frac{-\frac{\hbar^2}{2m}\int_0^\infty x\, e^{-\alpha x^2}\left[-2\alpha.2xe^{-\alpha x^2}+4\alpha^2x^3e^{-\alpha x^2}-2\alpha xe^{-\alpha x^2}\right]dx+\frac{1}{2}m\omega^2\frac{1}{2}\frac{\Gamma\left(\frac{5}{2}\right)}{(2\alpha)^{5/2}}}{\frac{1}{2}\frac{\Gamma\left(\frac{3}{2}\right)}{(2\alpha)^{3/2}}}$$

$$= \frac{-\frac{\hbar^2}{2m}\left[-6\alpha\int_0^\infty x^2e^{-2x^2\alpha}+4\alpha^2\int_0^\infty x^4e^{-2\alpha x^2}dx\right]}{\frac{1}{2}\times\frac{1}{2}\frac{\sqrt{\pi}}{(2\alpha)^{3/2}}}+\frac{\frac{3}{16}\frac{m\omega^2\sqrt{\pi}}{(2\alpha)^{5/2}}}{\frac{1}{4}\frac{\sqrt{\pi}}{(2\alpha)^{3/2}}}$$

$$= \frac{\frac{6\alpha\hbar^2}{2m}\frac{1}{2}\frac{\Gamma\left(\frac{3}{2}\right)}{(2\alpha)^{3/2}}-\frac{\hbar^2}{m}\frac{2\alpha^2}{2}\frac{\Gamma\left(\frac{5}{2}\right)}{(2\alpha)^{5/2}}}{\frac{1}{4}\frac{\sqrt{\pi}}{(2\alpha)^{3/2}}}+\frac{3}{4}\frac{m\omega^2}{(2\alpha)}$$

$$= \frac{6\alpha\hbar^2}{2m\times2}\times\frac{4(2\alpha)^{3/2}}{\sqrt{\pi}}\frac{1}{2}\frac{\sqrt{\pi}}{(2\alpha)^{3/2}}-\frac{\frac{\hbar^2}{m}\alpha^2\times\frac{3}{2}\sqrt{\pi}}{(2\alpha)^{5/2}}\times\frac{4(2\alpha)^{3/2}}{\sqrt{\pi}}+\frac{3}{4}\frac{m\omega^2}{2\alpha}$$

$$= \frac{6\alpha\hbar^2}{2\times m}-\frac{\hbar^2}{m}\alpha^2\frac{6}{2\times2\alpha}+\frac{3}{8}\frac{m\omega^2}{\alpha}=\frac{3\alpha\hbar^2}{m}-\frac{3}{2}\frac{\hbar^2\alpha}{m}+\frac{3}{8}\frac{m\omega^2}{\alpha}$$

$$\Rightarrow \quad \langle E\rangle=\frac{3}{2}\frac{\alpha\hbar^2}{m}+\frac{3}{8}\frac{m\omega^2}{\alpha} \qquad \Rightarrow \frac{\partial\langle E\rangle}{\partial\alpha}=\frac{3}{2}\frac{\hbar^2}{m}-\frac{3}{8}\frac{m\omega^2}{\alpha^2}$$

$$\Rightarrow \quad \frac{3}{2}\frac{\hbar^2}{m}-\frac{3}{8}\frac{m\omega^2}{\alpha^2}=0 \quad \Rightarrow \frac{1}{4}\frac{m\omega^2}{\alpha^2}=\frac{\hbar^2}{m}$$

$$\Rightarrow \quad \alpha^2=\frac{1}{4}\frac{m^2\omega^2}{\hbar^2} \quad \Rightarrow \quad \alpha=\frac{1}{2}\frac{m\omega}{\hbar}$$

$$\therefore \quad \langle E\rangle=\frac{3}{2}\frac{\hbar^2}{m}\left(\frac{1}{2}\frac{m\omega}{\hbar}\right)+\frac{3}{8}m\omega^2\left(\frac{2\hbar}{m\omega}\right)=\frac{3}{4}\hbar\omega+\frac{3}{4}\hbar\omega=\frac{3}{2}\hbar\omega$$

Problem: Use the variational method to calculate the ground state energy of a particle in the potential defined as

$$V(x)=\begin{cases}\infty & x\le 0\\ kx & x>0\end{cases}$$

Use trial wave function $\psi(x)=xe^{-\alpha x}$

Soln. $\psi(x) = xe^{-\alpha x}$

$$H = \frac{p^2}{2m} + kx = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + kx$$

$$\langle \hat{H} \rangle = \frac{\int \psi^* \hat{H} \psi dx}{\int \psi^* \psi dx} = \frac{\int_0^\infty xe^{-\alpha x} \cdot \left(\frac{-\hbar^2}{2m}\right) \frac{\partial^2}{\partial x^2}\left(xe^{-\alpha x}\right)}{\int_0^\infty x^2 e^{-2\alpha x} dx} + \frac{\int_0^\infty kx.x^2 e^{-2\alpha x} dx}{\int_0^\infty x^2 e^{-2\alpha x} dx}$$

$$= \frac{\frac{-\hbar^2}{2m} \int xe^{-\alpha x} \frac{\partial}{\partial x}\left\{x.e^{-\alpha x}(-\alpha) + e^{-\alpha x}\right\} dx}{\frac{\lfloor 2}{(2\alpha)^3}} + \frac{\int_0^\infty kx^3 e^{-2\alpha x}}{\frac{\lfloor 2}{(2\alpha)^3}} dx$$

$$= \frac{-\hbar^2}{2m} \times \frac{(2\alpha)^3}{2} \int_0^\infty xe^{-\alpha x}\left[-\alpha e^{-\alpha x} + \alpha^2 xe^{-\alpha x} - \alpha e^{-\alpha x}\right] dx + \frac{(2\alpha)^3}{2} \times k.\frac{3!}{(2\alpha)^4}$$

$$= \frac{-2\hbar^3\alpha^2}{m} \int_0^\infty \left[\alpha^2 x^2 e^{-2\alpha x} - 2\alpha x e^{-2\alpha x}\right] dx + \frac{3k \times 2}{2 \times 2\alpha}$$

$$= \frac{-2\hbar^2\alpha^3}{m}\left[\alpha^2 - \frac{\lfloor 2}{(2\alpha)^3} - 2\alpha.\frac{\lfloor 1}{(2\alpha)^2}\right] + \frac{3}{2}\frac{k}{\alpha} = \frac{2\hbar^2\alpha^3}{m}\left[\frac{1}{2\alpha} - \frac{1}{4\alpha}\right] + \frac{3}{2}\frac{k}{\alpha} = \frac{\hbar^2\alpha^2}{2m} + \frac{3}{2}\frac{k}{\alpha}$$

$$\frac{\partial \langle E \rangle}{\partial \alpha} = \frac{2\hbar^2\alpha}{2m} - \frac{3}{2}\frac{k}{\alpha^2}, \quad \frac{\hbar^2\alpha}{m} - \frac{3}{2}\frac{k}{\alpha^2} = 0, \quad \frac{\hbar^2}{m} = \frac{3}{2}\frac{k}{\alpha^2} \Rightarrow \alpha^3 = \frac{3km}{2\hbar^2} \Rightarrow \alpha = \left(\frac{3}{2}\frac{km}{\hbar^2}\right)^{1/3}$$

$$\alpha^3 = \frac{3km}{2\hbar^2}, \quad \alpha = \left(\frac{3mk}{2\hbar^2}\right)^{1/3}, \quad = \frac{\hbar}{4}\sqrt{\frac{3k}{2m}}$$

$$\langle E \rangle = \frac{\hbar^2}{2m}\alpha^2 + \frac{3}{2}\frac{k}{\alpha} = \frac{\hbar^2}{2m}\left(\frac{3mk}{2\hbar^2}\right)^{2/3} + \frac{3}{2}k\left(\frac{2\hbar^2}{3mk}\right)^{1/3}$$

$$= \frac{3^{2/3}}{2^{5/3}}\left(\frac{\hbar^2k^2}{m}\right)^{1/3} + \frac{3}{2}\left(\frac{2\hbar^2k^2}{3m}\right)^{1/3} = \frac{3}{2^2}\left(\frac{2\hbar^2k^2}{3m}\right)^{1/3} + \frac{3}{2}\left(\frac{2\hbar^2k^2}{3m}\right)^{1/3}$$

$$= \frac{3}{4}\left(\frac{2\hbar^2k^2}{3m}\right)^{1/3} + \frac{3}{2}\left(\frac{2\hbar^2k^2}{3m}\right)^{1/3} = \frac{9}{4}\left(\frac{2\hbar^2k^2}{3m}\right)^{1/3}$$

Problem : Use a Gausian trial function $\psi(x) = Ae^{-bx^2}$ (where b is variational parameter and A is normalisation constant) to obtain the lowest upper bound the ground state energy of

(i) The linear potential: $V(x) = \alpha|x|$ (ii) The linear potential: $V(x) = \alpha x^4$

Soln. (i) $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \alpha|x|$

$$\frac{d^2}{dx^2}e^{-bx^2} = \frac{d}{dx}\left[-2bxe^{-bx^2}\right] = -2b\left[e^{-bx^2} - 2bx^2e^{-bx^2}\right]$$

$$\hat{H}\psi = \frac{\hbar^2 b}{m}\left[e^{-bx^2} - 2bx^2e^{-bx^2}\right] + \alpha|x|$$

$$\langle\hat{H}\rangle = \frac{2\frac{\hbar^2 b}{m}\int_0^\infty\left(1-2bx^2\right)e^{-2bx^2}dx + \int_{-\infty}^{\infty}e^{-2bx^2}\alpha|x|dx}{2\int_0^\infty e^{-2bx^2}dx}$$

$$= \frac{\frac{2\hbar^2 b}{m}\left[\frac{1}{2}\frac{\Gamma\left(\frac{1}{2}\right)}{(2b)^{1/2}} - \frac{2b}{2}\frac{\Gamma\left(\frac{3}{2}\right)}{(2b)^{3/2}}\right] + 2\alpha\int_0^\infty e^{-2bx^2}xdx}{\frac{2}{2}\frac{\Gamma\left(\frac{1}{2}\right)}{(2b)^{1/2}}}$$

$$= \left[\frac{2\hbar^2 b}{m}\left[\frac{1}{2}\sqrt{\frac{\pi}{2b}} - \frac{b}{2}\frac{\sqrt{\pi}}{(2b)^{3/2}}\right] + \frac{2\alpha}{2}\frac{1}{(2b)}\right]\sqrt{\frac{2b}{\pi}}$$

$$\langle\hat{H}\rangle = \frac{2\hbar^2 b}{m}\left[\frac{1}{2} - \frac{1}{4}\right] + \frac{\alpha}{\sqrt{2b\pi}} = \frac{\hbar^2 b}{2m} + \frac{\alpha}{\sqrt{2b\pi}}$$

$$\frac{\partial\langle\hat{H}\rangle}{\partial b} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{1}{2}\frac{\alpha}{\sqrt{2\pi}}\frac{1}{b^{3/2}} = 0 \Rightarrow \frac{\hbar^2}{m\alpha}\sqrt{2\pi} = \frac{1}{b^{3/2}} \Rightarrow b^{3/2} = \frac{m\alpha}{\sqrt{2\pi}\hbar^2}$$

$$\Rightarrow b = \left(\frac{m\alpha}{\sqrt{2\pi}\,\hbar^2}\right)^{2/3}$$

$$\langle E\rangle = \frac{\hbar^2}{2m}\left(\frac{m\alpha}{\sqrt{2\pi}\,\hbar^2}\right)^{2/3} + \frac{\alpha}{\sqrt{2\pi}}\left(\frac{\sqrt{2\pi}\hbar^2}{m\alpha}\right)^{1/3} = \frac{1}{2}\left(\frac{\hbar^3\alpha m}{\sqrt{2\pi}\,m^{3/2}\hbar^2}\right)^{2/3} + \left(\frac{\alpha^3\hbar^2}{2\pi m\alpha}\right)^{1/3}$$

$$= \frac{1}{2}\left(\frac{\hbar\alpha}{\sqrt{2\pi m}}\right)^{2/3} + \left(\frac{\hbar^2\alpha^2}{2\pi m}\right)^{1/3} = \frac{3}{2}\left(\frac{\hbar^2\alpha^2}{2\pi m}\right)^{1/3}$$

(ii) $V = \alpha x^4 \quad \Rightarrow H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \alpha x^4$

$$\langle H\rangle = \frac{\frac{2\hbar^2 b}{m}\int_0^\infty (1-2bx^2)e^{-2bx^2}dx + 2\int_0^\infty \alpha x^4 e^{-2bx^2}dx}{2\int_0^\infty e^{-2bx^2}dx}$$

$$= \left[\frac{2\hbar^2 b}{2m}\left[\frac{1}{2}\sqrt{\frac{\pi}{2b}} - \frac{b}{2}\frac{\sqrt{\pi}}{(2b)^{3/2}}\right] + 2\alpha\frac{1}{2}\frac{\Gamma\left(\frac{5}{2}\right)}{(2b)^{5/2}}\right]\sqrt{\frac{2b}{\pi}} = \frac{\hbar^2 b}{2m} + \left[\alpha\frac{3}{2}\times\frac{1}{2}\frac{\sqrt{\pi}}{(2b)^{5/2}}\right]\sqrt{\frac{2b}{\pi}}$$

$$= \frac{\hbar^2 b}{2m} + \left[\frac{3}{4}\frac{\alpha}{(2b)^2}\right] = \frac{\hbar^2 b}{2m} + \frac{3}{16}\frac{\alpha}{b^2}$$

$$\frac{\partial\langle H\rangle}{\partial b} = \frac{\hbar^2}{2m} - \frac{3}{16}\frac{\alpha}{b^3}\times 2 \quad \Rightarrow \frac{\hbar^2}{2m} = \frac{3}{8}\frac{\alpha}{b^3} \quad \Rightarrow b^3 = \frac{3}{4}\frac{\alpha m}{\hbar^2} \quad \Rightarrow b = \left(\frac{3\alpha m}{4\hbar^2}\right)^{1/3}$$

$$\langle E\rangle = \frac{\hbar^2}{2m}\left(\frac{3\alpha m}{4\hbar^2}\right)^{1/3} + \frac{3\alpha}{16}\left(\frac{4\hbar^2}{3\alpha m}\right)^{2/3}$$

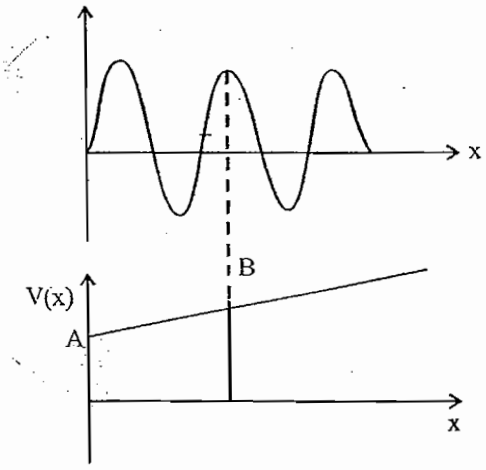
$$= \frac{1}{2}\left(\frac{3\hbar^6\alpha m}{4\hbar^2 m^3}\right)^{1/3} + \frac{1}{4}\left(\frac{3^{3/2}\times 4\hbar^2\alpha^{3/2}}{3\alpha m\times 4^{3/2}}\right) = \frac{1}{2}\left(\frac{3\hbar^4\alpha}{4m^2}\right)^{1/3} + \frac{1}{4}\left(\sqrt{\frac{3}{4}}\frac{\hbar^2\sqrt{\alpha}}{m}\right)^{2/3}$$

$$= \frac{1}{2}\left(\frac{3\hbar^2\alpha}{4m^2}\right)^{1/3} + \frac{1}{4}\left(\frac{3\hbar^2\alpha}{4m^2}\right)^{1/3} = \frac{3}{4}\left(\frac{3\hbar^2\alpha}{4m^2}\right)^{1/3}$$

WKB Method (Wentjel-Krammer-Brillouin Method)

Semi-Classical Approximation Method:

The WKB method is useful for appropriate treatment of system with slowly varying potential (the potential which remain constant over a region of the order of de-Broglie wavelength). One dimensional problem and also three dimensional problem reducible to one dimensional are solved by this method. It is called semiclassical method because for classical system wavlength tends to zero i.e. $\lambda \to 0$.



From A to B slope is negligible
So, V is slowly varying

As potential is slowly varying so variation of V for small region is almost zero.

Method: If potential is constant e.g. barrier, step, well etc.

$$V(x) = \text{constant}$$

$$\psi(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad \text{for } E > V$$

$$= Ae^{k_1x} + Be^{-k_1x} \qquad \text{for } E < V$$

But in WKB method $V(x)$ is not constant, it is slightly varying. So, there should be some modification in above wave function

As $k_1^2 = \frac{2m}{\hbar^2}[E - V]$

As potential is not constant i.e. $V = V(x)$

$$\therefore k_1^2 = \frac{2m}{\hbar^2}[E - V(x)]$$

So, wavefunction will be

In one dimension: $\psi(x) = A(x)e^{\frac{ip(x)x}{\hbar}}$ where $p(x) = \sqrt{2m(E - V(x))}$

In three dimension: $\psi(\vec{r}) = A(\vec{r})e^{\frac{i\vec{p}(\vec{r}).\vec{r}}{\hbar}}$

When we substitute this wavefunction in Schrodinger equation and solve.
We get corresponding amplitude etc. So, the wave function will be

For $E > V(x)$

$$\psi(x) = \frac{C_{+-}}{\sqrt{p(x)}}\exp\left[\frac{i}{\hbar}\int_0^x p(x')dx'\right] + \frac{C_-}{\sqrt{p(x)}}\exp\left[\frac{-i}{\hbar}\int_0^x p(x')dx'\right] \qquad \ldots(1)$$

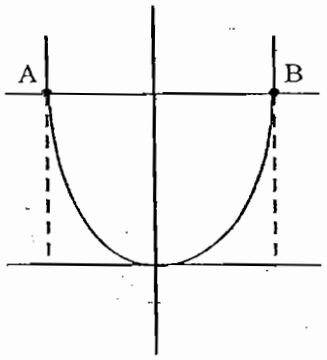
Here form of wave function is same, only amplitude and phase factor of wave function is changed.
For $E < V(x)$

$$\psi(x) = \frac{C_+}{\sqrt{p(x)}}\exp\left[\frac{1}{\hbar}\int_0^x p(x')dx\right] + \frac{C_-}{\sqrt{p(x)}}\exp\left[\frac{-1}{\hbar}\int_0^x p(x')dx'\right] \qquad \ldots(2)$$

Here the region $E > V(x)$ is known as classically allowed region and $E < V(x)$ is known as classically forbidden region.

What is the value of $\psi(x)$ at classical turning point i..e when

$E = V(x)$ then, $p(x) = 0$



A, B are classically turning point. i.e. on reaching these points, its motion will be backward classically.

When we put $p(x) = 0$ in eq^n.(1) & (2)

Then $\psi(x) \to \infty$

So, WKB method fails at classical turning point.
It is valid for both classical allowed and forbidden region but not at classical turning point.

Condition for validity of WKB Method:

$$\hbar\left|\frac{\frac{d^2s}{dx^2}}{\left|\frac{ds}{dx}\right|^2}\right| << 1, \qquad \left|\frac{d}{dx}\left(\frac{ds}{dx}\right)\right| << 1 \quad \text{As } \frac{ds}{dx} = p$$

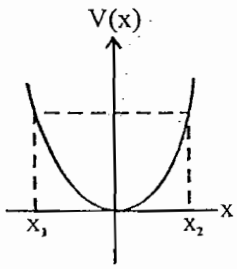
$$\therefore \quad \left|\frac{d}{dx}\left(\frac{\hbar}{p}\right)\right| << 1, \quad \text{As } \frac{\hbar}{p} = \lambda \qquad \Rightarrow \quad \left|\frac{d\lambda}{dx}\right| << 1$$

i.e. rate of change of wavelength w.r.t position is very less or wavelength of particle must vary slightly over the distances of the order of its size.

If we apply this condition at classical turning point as here $\lambda \to \infty$ then $\frac{d\lambda}{dx}$ is very large. So, method fails.

This condition breaks down at classical turning point because at classical turning point $p(x) = 0$ and $\lambda = \infty$ and voilate the requirement that λ remain small or varies slightly. WKB method is valid in both classically allowed and classically forbidden region but not at classical turning point.
We use another method to calculate behaviour of wave function at classical turning point, we expand the potential and neglecting higher order terms because potential is slightly varying

$$V(x) = V(x - x_2 + x_2) = V(x)\big|_{x=x_2} + (x - x_2)\frac{\partial V}{\partial x}\bigg|_{x=x_2}$$



As $V(x) =$ constant

$\therefore$ $V(x)$ will be linear as

$V(x) = mx + c$ type (straight line)

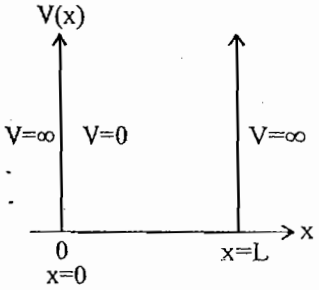
i.e. It gives straight line behaviour for any type of potential.

Problem: Use the WKB method to calculate the energy levels of a spin less particle of mass m moving in a one dimensional box with walls at $x = 0$ and $x = L$.

$V(x) = 0, \quad 0 < x < L$

$= \infty, \quad$ otherwise

Soln. Potential is:



As both boundary $x = 0$ and $x = L$ are rigid solution or wave function is given by

$$= \frac{D}{\sqrt{p(x)}} \sin\left[\frac{1}{\hbar}\int_0^L p(x')dx + \beta\right]$$

Quantisation condition:

$$\frac{1}{\hbar}\left[\int_0^L p(x')dx'\right] = n\pi \text{ where } n = 1,2,3.....$$

$$= (n+1)\pi \quad n = 0,1,2,3.....$$

Quantisation condition:

$$\int_0^L p(x')dx = n\pi\hbar \quad , n = 1,2,3.....$$

$$= (n+1)\pi\hbar \quad n = 0,1,2,.....$$

As $p(x) = \sqrt{2m(E - V(x))}$

As $V(x) = 0$

$\therefore$ $$\int_0^L \sqrt{2mE}\, dx = n\pi\hbar = (n+1)\pi\hbar$$

$$\sqrt{2mE}\,(L) = n\pi\hbar = (n+1)\pi\hbar$$

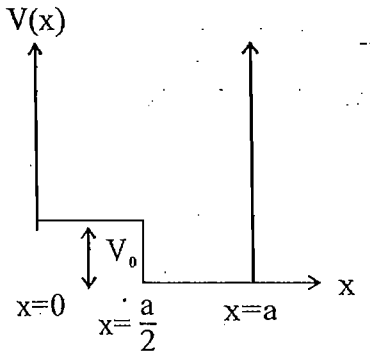
$$\Rightarrow \quad E = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n = 1,2,3.....$$

$$= \frac{(n+1)^2\pi^2\hbar^2}{2mL^2} \qquad n = 0,1,2,3.....$$

Problem: Use the WKB approximation to find the allowed energies of an infinite square well potential with a shelf of height V_0 extending half way across.

$$V(x) = \begin{cases} V_0 & \text{if } 0 < x < \frac{a}{2} \\ 0 & \frac{a}{2} < x < a \\ \infty & \text{otherwise} \end{cases}$$

Soln.



Quantisation condition:

$$\int_0^a p(x)\,dx = (n+1)\pi\hbar \qquad n = 0,1,2,.....$$

$$= n\pi\hbar \qquad n = 1,2,3,.....$$

Using value of p(x) :

$$\int_0^{a/2} \sqrt{2m(E-V_0)}\,dx + \int_{a/2}^{a} \sqrt{2mE}\,dx = n\pi\hbar$$

$$\Rightarrow \quad \sqrt{2m(E-V_0)}\,[x]_0^{a/2} + \sqrt{2mE}\,[x]_{a/2}^{0} = n\pi\hbar$$

$$\Rightarrow \quad \sqrt{2m(E-V_0)}\left(\frac{a}{2}\right) + \sqrt{2mE}\,\frac{a}{2} = n\pi\hbar$$

$$\Rightarrow \quad \sqrt{2m}\,\frac{a}{2} + \left[\sqrt{E-V_0} + \sqrt{E}\right] = n\pi\hbar$$

$$\Rightarrow \quad \left(\sqrt{E-V_0} + \sqrt{E}\right)^2 = \left(\frac{2}{a}\frac{n\pi\hbar}{\sqrt{2m}}\right)^2$$

$$\Rightarrow \quad E-V_0+E+2\sqrt{E(E-V_0)}=\frac{4n^2\pi^2\hbar^2}{2ma^2}$$

$$\Rightarrow \quad 2E-V_0+2\sqrt{E(E-V_0)}=4\left(\frac{n^2\pi^2\hbar^2}{2ma^2}\right)$$

$$\Rightarrow \quad 2E-V_0+2\sqrt{E(E-V_0)}=4E_n^{(o)}$$

$$\Rightarrow \quad 2E-V_0-4E_n^{(o)}=2\sqrt{E(E-V_0)}$$

$$\left(2\left(E-2E_n^{(0)}\right)-V_0\right)^2=4E(E-V_0)$$

$$\Rightarrow \quad 4\left[E^2+4\left(E_n^0\right)^2-4EE_n^0\right]+V_0^2-4V_0\left(E-2E_n^0\right)=4E(E-V_0)$$

$$\Rightarrow \quad 4E^2+16\left(E_n^0\right)^2-16EE_n^0+V_0^2-4V_0E+8V_0E_n^0=4E^2-EV_0$$

$$\Rightarrow \quad 16EE_n^0=16\left(E_n^0\right)^2+8E_n^0V_0+V_0^2$$

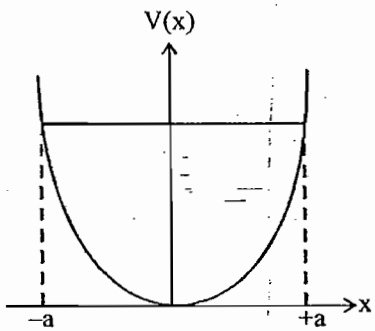
$$\Rightarrow \quad E=\frac{1}{16E_n^0}\left[16\left(E_n^0\right)^2+8E_n^0V_0+V_0^2\right]$$

$$\Rightarrow \quad E_{WKB}=E_n^0+\frac{V_0}{2}+\frac{V_0^2}{16E_n^0}$$

Problem: Use the WKB aproximation to calculate the energy of a one-dimensional harmonic oscillation or defined as $V(x)=\frac{1}{2}m\omega^2x^2$

Soln. Here -a and +a are two turning points both are at non rigid walls.

$$\therefore \quad \alpha=\frac{\pi}{4}$$



$$\psi(x)=\frac{D}{p(x)}\sin\left\{\frac{1}{\hbar}\int_{x_1}^{x_2}p(x)dx+\alpha\right\}$$

$x_1 \le x \le x_2$

Considering argument only

$$\left[\frac{1}{\hbar}\int_{-a}^{0}p(x)dx+\alpha+\frac{1}{\hbar}\int_{0}^{a}p(x)dx+\alpha\right]=(n+1)\pi \qquad n=0,1,2,.....$$

As both the walls are rigid.

$$\left[\frac{1}{\hbar}\int_{-a}^{0}p(x)dx+\frac{\pi}{4}+\frac{1}{\hbar}\int_{0}^{a}p(x)dx+\frac{\pi}{4}\right]=(n+1)\pi$$

$$\int_{-a}^{a}p(x)dx+\frac{\pi}{2}\hbar=(n+1)\pi\hbar \quad \Rightarrow \quad \int_{-a}^{a}p(x)dx=\left(n+\frac{1}{2}\right)\pi\hbar$$

$$p=\sqrt{2m\left(E-V(x)\right)}=\sqrt{2m\left(E-\frac{1}{2}m\omega^2x^2\right)}$$

As at turning point E = P.E. $\quad E=\frac{1}{2}m\omega^2a^2$

$$p=\sqrt{2m\left(\frac{1}{2}m\omega^2a^2-\frac{1}{2}m\omega^2x^2\right)}=m\omega\sqrt{a^2-x^2}$$

$$\therefore \quad \int_{-a}^{a} m\omega\sqrt{a^2-x^2}\,dx=\left(n+\frac{1}{2}\right)\pi\hbar$$

$x=a\cos\theta \qquad x=a\sin\theta$

$dx=a\sin\theta d\theta \qquad dx=a\cos\theta d\theta$

$x=a;\theta=0 \qquad x=-a,\ \theta=\frac{3\pi}{2}$

$x=-a;\theta=\pi \qquad x=a,\ \theta=\frac{\pi}{2}$

$$\int_0^{\pi} m\omega\sqrt{a^2-a^2\cos^2\theta}\ a\sin\theta d\theta=\left(n+\frac{1}{2}\right)\pi\hbar$$

$$\Rightarrow \quad \frac{m\omega a^2}{2}\int_0^{\pi}2\sin^2\theta d\theta=\left(n+\frac{1}{2}\right)\pi\hbar$$

$$\Rightarrow \quad \frac{m\omega a^2}{2}\int_0^{\pi}\left(\frac{1-\cos 2\theta}{2}\right)d\theta=\left(n+\frac{1}{2}\right)\pi\hbar$$

$$\Rightarrow \quad \frac{m\omega a^2}{2}\left[\theta-\frac{\sin 2\theta}{2}\right]_0^{\pi}=\left(n+\frac{1}{2}\right)\pi\hbar$$

$$\Rightarrow \quad \frac{E}{\omega}[\pi]=\left(n+\frac{1}{2}\right)\pi\hbar$$

$$\Rightarrow \quad E=\left(n+\frac{1}{2}\right)\hbar\omega \qquad n=0,1,2,.....$$

UNIT-IX
RELATIVISTIC QUANTUM MECHANICS

In this we include the concepts of relativity along with the concepts of quantum mechanics

Klein Gorden Equation :

Schrodinger equation, $\hat{H}\psi = i\hbar\frac{\partial\psi}{dt}$

non-relativistic Schrodinger equation, $\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r},t) = i\hbar\frac{\partial\psi}{dt}(\vec{r},t)$ ...(1)

This equation is invariant under linear transformation of space co-ordinates alone, but not invariant under Lorentz transformation. This is due to as we use non-relativistic Hamiltonian.

$$\hat{H} = E = \pm\sqrt{c^2p^2 + m^2c^4}$$

The Schrodinger equation, $\left(\pm\sqrt{c^2p^2 + m^2c^4}\right)\psi = i\hbar\frac{\partial\psi}{dt}$ ...(2)

There are two difficulties:

First difficulty is related to interpret sign $\pm$. There is no problem in classical mechanics since energy can continuously vary with a gap of $2mc^2$ between lowest positive & highest negative value. If any particle has any type of energy other can be ignored. But in quantum mechanics energy can change discontinuously.

Second difficulty : If $\left[-\hbar^2c^2\nabla^2 + m^2c^4\right]^{1/2} = i\hbar\frac{\partial\psi}{dt}$

We can not interpret the square root of any operator and if we expand it binomially there will be space & time derivative in unsymmetrical form, so it will not Lorentz invariant and will be difficult to solve.

Klein-Gorden modified this Schrodinger equation

$$H\psi = i\hbar\frac{\partial\psi}{dt}$$

$$H^2\psi = i\hbar\hat{H}\frac{\partial\psi}{dt} = i\hbar\frac{\partial}{dt}\hat{H}\psi$$

$$\boxed{H^2\psi = -\hbar^2\frac{\partial^2\psi}{dt^2}}$$

This equation is relativistic Schrodinger equation and also known as Klein-Gordan equation for a relativestic free particle Klein-Gordan equation

$$\boxed{\left(-\hbar^2c^2\nabla^2 + m^2c^4\right)\psi = -\hbar^2\frac{\partial\psi}{dt^2}}$$

$$\Rightarrow \left[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{dt^2} - \frac{m^2c^4}{\hbar^2}\right]\psi = 0 \Rightarrow \left[\Box^2 - \frac{m^2c^4}{\hbar^2}\right]\psi = 0 \quad \left(\text{Here } \Box^2 = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{dt^2}\right)$$

$$\Rightarrow \boxed{\left[g^{\mu\upsilon}\frac{\partial}{\partial x^{\upsilon}}\frac{\partial}{\partial x_{\upsilon}} - k^2\right]\psi\left(x^{\alpha}\right) = 0} \quad \left(\text{Here } g^{\mu\upsilon} = \begin{cases} 1 & \text{if } \mu = \upsilon \\ 0 & \mu \neq \upsilon \end{cases}\right)$$

Charge and current densities : Klein-Gordan equation for free particle

$$\nabla^2\psi - \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} - \frac{m^2c^4}{\hbar^2}\psi = 0 \qquad \ldots (1)$$

$$\nabla^2\psi^* - \frac{1}{c^2}\frac{\partial^2\psi^*}{\partial t^2} - \frac{m^2c^4\psi^*}{\hbar^2} = 0 \qquad \ldots (2) \quad \text{(On taking complex conjugate)}$$

$$\left.\begin{aligned} \psi^* \times (1) \quad &\Rightarrow \psi^*\nabla^2\psi - \frac{1}{c^2}\psi^*\frac{\partial^2\psi}{dt^2} - \frac{m^2c^4}{\hbar^2}\psi^*\psi = 0 \\ \psi \times (2) \quad &\Rightarrow \psi\nabla^2\psi^* - \frac{1}{c^2}\frac{\partial^2\psi^*}{\partial t^2} - \frac{m^2c^4}{\hbar^2}\psi\psi^* = 0 \end{aligned}\right] \qquad \ldots (3)$$

From equation (3),

$$\Rightarrow \quad \psi^*\nabla^2\psi - \psi\nabla^2\psi^* - \frac{1}{c^2}\left[\psi^*\frac{\partial^2\psi}{\partial t^2} - \psi\frac{\partial^2\psi^*}{\partial t^2}\right] = 0$$

$$\Rightarrow \quad \nabla.\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right] - \frac{1}{c^2}\left[\psi^*\frac{\partial^2\psi}{\partial t^2} - \psi\frac{\partial^2\psi^*}{\partial t^2}\right] = 0$$

$$\Rightarrow \quad \nabla.\left[\frac{-i\hbar}{2m}\left\{\psi^*\nabla\psi - \psi\nabla\psi^*\right\}\right] + \frac{\partial}{\partial t}\left[\frac{-i\hbar}{2mc^2}\left\{\psi^*\frac{\partial\psi}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right\}\right] = 0 \qquad \ldots(4)$$

$$\boxed{\nabla.\bar{S}(\vec{r},t) + \frac{\partial P}{\partial t}(\vec{r},t) = 0} \qquad \ldots(5)$$

Equation of continuity & $\bar{S}(\vec{r},t) = \frac{-i\hbar}{2m}\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right]$

$$P(\vec{r},t) = \frac{-i\hbar}{2mc^2}\left[\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right] = \frac{1}{2mc^2}\left[\left(-i\hbar\frac{\partial\psi^*}{\partial t}\right)\psi^*\left(i\hbar\frac{\partial\psi}{\partial t}\right)\right]$$

$$= \frac{1}{2mc^2}\left[\left(E\psi^*\right)\psi + \psi^*E\psi\right]$$

Using Schrodinger equation $\left(H\psi = i\hbar\frac{\partial\psi}{\partial t} = E\psi\right)$ $\qquad P(\vec{r},t) = \frac{E}{2mc^2}\psi^*\psi$

Since $E = \pm\sqrt{c^2p^2 + m^2c^4}$ may be +ve or - ve

So $P(\vec{r},t)$ is not positive always hence it can not be regarded as conventional position probability density according to new interpretation of ψ by Pauli and Wesskopt

$eP \rightarrow$ charge density e may be +ve or – ve

$eS \rightarrow$ current density

Note : In K.G. equation ψ has one component (scalar). It ψ has more component (more degree of freedom) then these component shows spin motions. In the absence of other components, K.G. equation will describe particles of zero spin (like mesons) only.

In non relativistic case $E' << mc^2$, $P(\vec{r},t)$ in K.G. equation reduces to non relativistic probability density $\psi^*\psi$

Klein-Gordan Equation in electromagnetic field :

The relativistic energy

$$E^2 = c^2p^2 + m^2c^4$$

For a charge particle of charge q in the electromagnetic field corresponding to vector potential $\vec{A}$ and scalar potential ϕ the momentum $\vec{p} \to \vec{p} - \frac{q\vec{A}}{c}$ and energy $E \to E - q\phi$

$$H^2\psi = E^2\psi \quad \Rightarrow \left(c^2p^2 + m^2c^4\right)\psi = E^2\psi$$

$$\Rightarrow \quad \left[c^2\left(\vec{p} - \frac{q\vec{A}}{c}\right)^2 + m^2c^4\right]\psi = \left(E - q\phi\right)^2\psi$$

$$\Rightarrow \quad \left[c^2\left(-i\hbar\vec{\nabla} - \frac{q\vec{A}}{c}\right)^2 + m^2c^4\right]\psi = \left(i\hbar\frac{\partial}{\partial t} - q\phi\right)^2\psi$$

$$\Rightarrow \quad \left[\left(-i\hbar\vec{\nabla} - q\vec{A}\right)^2 + m^2c^4\right]\psi = \left(i\hbar\frac{\partial}{\partial t} - q\phi\right)^2\psi$$

Dirac's Relativistic Equation :

Dirac formulated an equation to avoid the difficulties arising in K-G equation on the basis of requirements of Lorentz in variance which demand that an equation which is linear in H an & hence in E must also be linear in p as in four momentum E and p are linear

The simplest linearized Hamiltonian for a free particle is :

$$\hat{H} = C\,\vec{\alpha}.\vec{p} + \beta mc^2$$

Where $\vec{\alpha}$ & β are independent of E & $\vec{p}$ (thus commutes with $\vec{r}$)

Since energy of a free particle is independent of position & t, so $\vec{\alpha}$ & β must be independent of $\vec{r}$ & t.

Thus component of $\vec{\alpha}$ & β commute with $\vec{p}$. $\vec{\alpha}$ & β not commute each after.

The Dirac's equation for free particle

$$\left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\psi = E\psi$$

$$\left(c\,\alpha_x p_x + c\,\alpha_y p_y + c\,\alpha_z p_z + \beta mc^2\right) = E\psi$$

where $p_x = -i\hbar\frac{\partial}{\partial x}$, $p_y \to -i\hbar\frac{\partial}{\partial y}$, $p_z = -i\hbar\frac{\partial}{\partial z}$

$\alpha_x, \alpha_y, \alpha_z$ & β have the following properties

(i) their squares are unity, $\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1$

(ii) $\alpha_x\alpha_y + \alpha_y\alpha_x = 0, \alpha_y\alpha_z + \alpha_z\alpha_y = 0, \quad \alpha_z\alpha_x + \alpha_x\alpha_z = 0,$

$$\alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_y\beta + \beta\alpha_z = 0$$

They anticommute with one another in pair current density

$\vec{\alpha}$ & β can be represented by matrices

$$\alpha_x = \begin{bmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{bmatrix} \quad \alpha_y = \begin{bmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{bmatrix} \quad \alpha_z = \begin{bmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{bmatrix}$$

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

where σ_x, σ_y & σ_z are Pauli's spin matrices.

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Probability density and current density in Dirac equation :

Dirac equation for a free particles is :

$$\left[E - c\,\vec{\alpha}.\vec{p} - \beta m c^2\right]\psi = 0$$

$$i\hbar\frac{\partial\psi}{\partial t} + i\hbar c\,\vec{\alpha}.\vec{\nabla}\psi - \beta m c^2\psi = 0 \qquad \ldots (1)$$

$$-i\hbar\frac{\partial\psi}{\partial t} + -i\hbar c\,\vec{\nabla}\psi^\dagger.\vec{\alpha} - \psi^\dagger\beta m c^2 = 0 \qquad \text{on taking Hermitian conjugatge}$$

multing (1) by $\psi^\dagger$ on the left & (2) by ψ on right & substracting

$$i\hbar\psi^\dagger\frac{\partial\psi}{\partial t} + i\hbar\psi^\dagger c\,\vec{\alpha}.\nabla\psi - m c^2\psi^\dagger\beta\psi - i\hbar\frac{\partial\psi}{\partial t}\psi + i\hbar\, c\vec{\nabla}\psi^\dagger.\vec{\alpha}\psi + \psi^\dagger\beta m c^2 = 0$$

$$i\hbar\frac{\partial}{\partial t}\left(\psi^\dagger\psi\right) + i\hbar\, c\vec{\nabla}.\left(\psi^\dagger\vec{\alpha}\psi\right) = 0$$

$$\nabla.S + \frac{\partial P}{\partial t} = 0$$

$P(\vec{r},t) = \psi^\dagger\psi$ ← probability density

$S(\vec{r},t) = c\psi^\dagger\vec{\alpha}\psi$ ← current density

$= \psi^\dagger\vec{v}\psi$ where $\vec{v} = c\vec{\alpha}$ → velocity of the particle

Problem. If $\vec{\alpha}$ represents three Dirac matrices $\alpha_x, \alpha_y, \alpha_z$ & $\vec{B}$ & $\vec{C}$ are usual three dimensional vectors then show that $\left(\vec{\alpha}.\vec{B}\right)\left(\vec{\alpha}.\vec{C}\right) = \vec{B}.\vec{C} + i\,\vec{\sigma}'.\vec{B}\times\vec{C}$ where $\vec{\sigma}' = \begin{bmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{bmatrix}$ is 4×4 matrix, $\vec{\sigma}$ being 2×2 Pauli spin matrix

Soln. $\left(\vec{\alpha}.\vec{B}\right)\left(\vec{\alpha}.\vec{C}\right) = \left(\alpha_x B_x + \alpha_y B_y + \alpha_z B_z\right)\left(\alpha_x C_x + \alpha_y C_y + \alpha_z C_z\right)$

$$= \alpha_x B_x\alpha_x c_x + \alpha_y B_y\alpha_y c_y + \alpha_z B_z\alpha_z c_z + \alpha_x B_x\alpha_y c_y + \alpha_x B_x\alpha_z c_z + \alpha_y B_y\alpha_x c_x + \alpha_y B_y\alpha_z c_z + \alpha_z B_z\alpha_x c_x + \alpha_z B_z\alpha_y c_y$$

$$= \alpha_x^2 B_x c_x + \alpha_y^2 B_y c_y + \alpha_z^2 B_z c_z + \alpha_x\alpha_y B_x c_y + \alpha_x\alpha_z B_x c_z + \alpha_y\alpha_x B_y c_x + \alpha_y\alpha_z B_y c_z + \alpha_z\alpha_x B_z c_x + \alpha_z\alpha_y B_z c_y$$

$$= B_x C_x + B_y C_y + B_z C_z + \alpha_x\alpha_y(B_x B_y - B_y B_x) + \alpha_y\alpha_z(B_y C_z - B_z C_y) + \alpha_z\alpha_x\left(B_z C_x - B_x C_z\right)$$

Using $\left(\alpha_x\alpha_y + \alpha_y\alpha_x = 0,\ \alpha_x^2 = 1\ \alpha_y^2 = 1 = \alpha_z^2\right)$

$$\left(\vec{\alpha}.\vec{B}\right)\left(\vec{\alpha}.\vec{C}\right) = \left(\vec{B}.\vec{C}\right) + i\sigma_z'\left(B_x B_y - B_y B_x\right) + i\sigma_x'\left(B_y C_z - B_z C_y\right) + i\sigma y'\left(B_z C_x - B_x C_z\right)$$

$$= \vec{B}.\vec{C} + i\vec{\sigma}'.\left(\vec{B}\times\vec{C}\right)$$

Problem: If $\vec{\alpha}$ and $\vec{\beta}$ are Dirac matrices, prove that :

(i) $\alpha_x = \frac{1}{2}\left[\alpha_x\alpha_y, \alpha_y\right]$ (ii) $\alpha_x\alpha_y\alpha_z = \frac{1}{2}\left[\alpha_x\alpha_y\alpha_z\beta, \beta\right]$

(iii) Trace $\left(\vec{\alpha}.\vec{\beta}\right)\left(\vec{\alpha}.\vec{C}\right) = 4\vec{B}.\vec{C}$ where $\vec{B}$ & $\vec{C}$ are three dim. vectors.

Soln. (i) $\left[\alpha_x\alpha_y, \alpha_y\right] = \alpha_x\alpha_y\alpha_y - \alpha_y\alpha_x\alpha_y$

$$\left[\alpha_x\alpha_y,\alpha_y\right]=\alpha_x\alpha_y\alpha_y-\alpha_y\alpha_x\alpha_y=\alpha_x-\left(\alpha_x\alpha_y\right)\alpha_y=\alpha_x+\alpha_x\alpha_y^2=2\alpha_x$$

$$\alpha_x=\frac{1}{2}\left[\alpha_x\alpha_y,\alpha_y\right]$$

(ii) $\left[\alpha_y\alpha_y\alpha_z\beta,\beta\right]=\alpha_x\alpha_y\alpha_z\beta\beta-\beta\alpha_x\alpha_y\alpha_z\beta=\alpha_x\alpha_y\alpha_z\beta^2+\alpha_x\beta\alpha_y\alpha_z\beta$

$$=\alpha_x\alpha_y\alpha_z+\alpha_x\alpha_y\alpha_z\beta^2=2\alpha_x\alpha_y\alpha_z$$

$$\alpha_x\alpha_y\alpha_z=\frac{1}{2}\left[\alpha_x\alpha_y\alpha_z\beta,\beta\right]$$

(iii) $\left(\vec{\alpha}.\vec{B}\right)\left(\vec{\alpha}.\vec{C}\right)=\alpha^2B_xC_x+\alpha_y^2B_yC_y+\alpha_z^2B_zC_z+\alpha_x\alpha_y\left(B_xC_y-B_yC_x\right)$

$$+\alpha_z\alpha_x\left(B_zC_x-B_xC_z\right)+\alpha_y\alpha_z\left(B_yC_z-B_zC_y\right)$$

$$\alpha_x^2=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{bmatrix}=\alpha_y^2=\alpha_z^2,\quad \alpha_x\alpha_y=\begin{bmatrix}i&0&0&0\\0&-i&0&0\\0&0&i&0\\0&0&0&-i\end{bmatrix},\quad \sigma_z\alpha_x=\begin{bmatrix}0&1&0&0\\-1&0&0&0\\0&0&0&1\\0&0&-1&0\end{bmatrix},$$

$$\alpha_y\alpha_x=\begin{bmatrix}0&i&0&0\\i&0&0&0\\0&0&0&i\\0&0&i&0\end{bmatrix}$$

$$(\vec{\alpha}.\vec{B})(\vec{\alpha}.\vec{C})=4\left(B_xC_x+3_yC_y+B_zC_z\right)+0+0+0=4\left(\vec{B}.\vec{C}\right)$$